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[54] Insecticidal N'-substituted-N-alkylcarbonyl-N'-acyl hydrazines.

N'-substituted-N-alkylcarbonyl-N'-acyl-hydrazines are new insecticidal compounds and are especially useful, for example in compositions also containing agronomically acceptable diluent or carrier in combating insects of the orders Lepidoptera and Coleoptera. The compounds have the formula:

wherein

X and X' are the same or different O, S or NR;

R1 is unsubstituted (C1-C10) branched alkyl or (C1-C4) straight chain alkyl substituted with one or two of the same or different (C₃-C₆) cycloalkyl;

A is unsubstituted or substituted (C1-C10) alkyl unsubstituted or substituted saturated or unsaturated (C3-C8) cyclo-alkyl or (C₃-C₆) cycloalkyl-(C₁-C₄) alkyl unsubstituted or substituted (C2-C8) alkynyl phenalkyl having one to four carbon atoms in the alkyl group and the phenyl ring is unsubstituted or substituted

B is unsubstituted or substituted naphthyl or phenyl and agronomically acceptable salts thereof.

INSECTICIDAL N'-SUBSTITUTED-N-ALKYLCARBONYL-N'-ACYL HYDRAZINES

This invention relates to N'-substituted-N-alkyl-carbonyl-N'-acylhydrazines which are useful as insecticides, compositions containing those compounds and their use as insecticides.

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The search for compounds which have a combination of excellent insecticidal activity and low desirable toxicity is a continuing one because of factors such as the need for compounds exhibiting greater activity, better selectivity, low undesirable environmental impact, low production cost and effectiveness against insects resistant to many known insecticides.

Compounds of the present invention are particularly suitable for controlling plant-destructive insects in crops of cultivated plants, ornamentals and forestry.

Certain hydrazine and/or hydrazide derivatives have been disclosed in the literature.

In 25 <u>Aust. J. Chem.</u>, 523-529 (1972), several N,N'-dibenzoylhydrazine derivatives are disclosed in which one or both nitrogen atoms are alkylated or phenylated. No biological activity is disclosed for those compounds.

In 61 Helv. Chim. Acta, 1477-1510 (1978), several N,N'-dibenzoylhydrazine and hydrazide derivatives are disclosed. No biological activity is disclosed for those compounds.

In 44 <u>J.A.C.S.</u>, 2556-2567 (1922), isopropyl hydrazine (CH_3) $_2\text{CH-NH-NH}_2$, symmetrical diisopropyl hydrazine, dibenzoylisopropyl hydrazine and certain derivatives are disclosed. No biological activity is disclosed for those compounds.



In 44 <u>J.A.C.S.</u>, 1557-1564 (1972), isopropyl, menthyl and bornyl semicarbazides are disclosed. No biological activity is disclosed for those compounds.

In 48 J.A.C.S., 1030-1035 (1926), symmetrical di-methylphenylmethyl hydrazine and certain related compounds including 1,2-bis-methylphenylmethyl-4-phenyl-semicarbazide are disclosed. No biological activity is disclosed for those compounds.

In 27 <u>Bull. Chem. Soc. Japan</u>, 624-627 (1954), certain hydrazine derivatives including alpha, beta-dibenzoylphenyl hydrazine are disclosed. No biological activity is disclosed for those compounds.

In <u>J. Chem. Soc. (C)</u>, 1531-1536 (1966), N,N'-dibenzoylphenyl hydrazine and N-acetyl-N'-benzoyl-p-nitrophenyl hydrazine are disclosed. No biological activity is disclosed for those compounds.

In 56B Chem. Berichte, 954-962 (1923), symmetrical di-isopropyl hydrazines, symmetrical diisobutyl and certain derivatives including N,N'-di-isobutyldibenzoyl hydrazine are disclosed. No biological activity is disclosed for those compounds.

In 590 Annalen der Chemie, 1-36 (1954), certain N,N'-dibenzoyl hydrazine derivatives are disclosed including N'-methyl- and N'-(2-phenyl)-isopropyl-N,N'-dibenzoyl hydrazine. No biological activity is disclosed for those compounds.

In <u>J. Chem. Soc.</u>, 4191-4198 (1952), N,N'-di-<u>n</u>-propyl hydrazine and the bis-3,5-dinitrobenzoyl derivatives are disclosed. No biological activity is disclosed for those compounds.

In 32 Zhur. Obs. Khim., 2806-2809 (1962), N'-2,4-methyl-2,4-pentadiene-N,N'-dibenzoyl hydrazine is disclosed. No biological activity is disclosed.

In 17 Acta. Chim. Scand., 95-102 (1963), 2-benzoyl-thiobenzhydrazide (${\rm C_6^H}_5$ -CS-NHNH-CO- ${\rm C_6^H}_5$) and

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certain hydrazone and hydrazine derivatives are disclosed including 1,2-dibenzoyl-benzyl hydrazine. No biological activity is disclosed for those compounds.

In 25 Zhur. Obs. Khim, 1719-1723 (1955), N,N'-bis-cyclohexyl hydrazine and N,N'-dibenzoylcyclohexyl hydrazine are disclosed. No biological activity is disclosed for those compounds.

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In <u>J. Chem. Soc.</u>, 4793-4800 (1964), certain dibenzoyl hydrazine derivatives are disclosed including tribenzoyl hydrazine and N,N'-dibenzoylcyclohexyl hydrazine. No biological activity is disclosed for those compounds.

In 36 <u>J. Prakt. Chem.</u>, 197-201 (1967), certain dibenzoyl hydrazine derivatives including N'-ethyl-; N'-n-propyl-; N'-isobutyl-; N'-neopentyl-; N'-n-heptyl-; and N'-cyclohexylmethyl-N,N'-dibenzoyl hydrazines are disclosed. No biological activity is disclosed for those compounds.

In 26 <u>J.O.C.</u>, 4336-4340 (1961) N'-<u>t</u>-butyl-N,N'-di-(<u>t</u>-butoxycarbonyl) hydrazide is disclosed. No biological activity is disclosed.

In 41 <u>J.O.C.</u>, 3763-3765 (1976), $N'-\underline{t}$ -butyl-N-(phenylmethoxycarbonyl)-N'-(chlorocarbonyl)hydrazide is disclosed. No biological activity is disclosed.

In 94 <u>J.A.C.S.</u>, 7406-7416 (1972) N'-<u>t</u>-butyl-N,N'-dimethoxycarbonyl hydrazide is disclosed. No biological activity is disclosed.

In 43 <u>J.O.C.</u>, 808-815 (1978), N'- \underline{t} -butyl-N-ethoxycarbonyl-N'-phenylaminocarbonyl-hydrazide and N'- \underline{t} -butyl-N-ethoxycarbonyl-N'-methylaminocarbonyl hydrazide are disclosed. No biological activity is disclosed for those compounds.

In 39 <u>J. Econ. Ent.</u>, 416-417 (1946), certain N-phenyl-N'-acylhydrazines are disclosed and evaluated for their toxicity against codling moth larvae.

The N'-substituted-N-alkylcarbonyl-N'-acryl-hydrazines of the present invention differ from known compounds primarily by their N- and N'-substituents.

Compounds of the present invention are distinguished by their excellent insecticidal activity against insects of the orders Lepidoptera and Coleoptera.

In accordance with the present invention, there are provided insecticidal compounds, compositions containing them and methods of using such compounds and compositions wherein the compounds are those having the formula:

wherein

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X and X' are the same or different O, S or NR;

- R^1 is unsubstituted (C_3-C_{10}) branched alkyl or (C_1-C_4) straight chain alkyl substituted with one or two of the same or different (C_3-C_6) cycloalkyl;
 - A is unsubstituted or substituted (C_1-C_{10}) alkyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH₂, NHZ or NZZ';

unsubstituted or substituted (C_3-C_8) cycloalkyl or (C_3-C_8) cycloalkyl- (C_1-C_4) alkyl having one to four of the same or

different halo, cyano, nitro, hydroxy, $(C_1-C_4) \text{ alkyl}, \text{ halo } (C_1-C_4) \text{ alkyl}, \text{ } (C_1-C_4)-\text{ alkoxy}, \text{ halo } (C_1-C_4) \text{ alkoxy}, \text{ carboxy}, \\ (C_1-C_4) \text{ alkanoyl}, \text{ } (C_1-C_4) \text{ alkoxy-carbonyl}, \\ (C_1-C_4) \text{ alkanoyloxy}, \text{ NHZ OR NZZ'};$

unsubstituted or substituted (C_2-C_8) alkenyl or unsubstituted or substituted (C_2-C_8) - alkadienyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, (C_3-C_6) cycloalkyl, halo- (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH₂, NHZ or NZZ';

unsubstituted or substituted (C_3-C_8) cycloalkenyl or unsubstituted or substituted (C_3-C_8) cycloalkadienyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH2, NHZ or NZZ';

unsubstituted or substituted (C_2-C_8) alkynyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo- (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH₂, NHZ or NZZ'; or

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phenalkyl having one to four carbon atoms in the alkyl group and the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, cyano (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, (C_2-C_6) alkenyl, halo (C_2-C_6) alkenyl, NHz or NZZ';

B is unsubstituted or substituted naphthyl where the substituents can be from one to three of the same or different halo; cyano; nitro; hydroxy; (C₁-C₄)alkoxy; (C₁-C₄)-alkyl; carboxy; (C₁-C₄)alkoxy-carbonyl; (C₁-C₄)alkanoyloxy; NH₂, NHZ or NZZ';

unsubstituted or substituted phenyl where the substituents can be from one to five of the same or different halo; nitro; cyano; hydroxy; (C₁-C₆)alkyl; halo(C₁-C₆)alkyl; cyano(C₁-C₆)alkyl; (C₁-C₆)alkoxy; halo-(C₁-C₆)alkoxy; alkoxyalkyl having independently 1 to 6 carbon atoms in each alkyl group; alkoxyalkoxy having independently 1 to 6 carbon atoms in each alkyl group; (-OCO₂R) group; (C₂-C₆)alkenyl

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optionally substituted with halo, cyano, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkoxy or (C₁-C₄)alkylthio; -RCO₂R' group; -COR group; halo(C₁-C₆)alkyl-carbonyl; cyano(C_1 - C_6) alkyl-carbonyl; nitro (C_1 - C_6)alkyl-carbonyl; $-CO_2R$ group; halo(C_1-C_6)alkoxy-carbonyl; -OCOR group; -NRR' group; amino substituted with hydroxy, (C_1-C_4) alkoxy or (C_1-C_4) alkylthio groups; phenylamino; diphenylamino; -CONRR' group; -OCONRR' group; -NRCOR' group; -NRCO2R' group; -N(COR)COR' group; -OCONRCOR' group; sulfhydryl; halothio; (C₁-C₆)alkylthio; halo(C₁-C₆)alkylthio; sulfinyl -SOR group; -SO₂R group; phenylsulfonyl; -OSO₂R group; halo(C₁-C₆)alkylsulfonyloxy; -SO₂NRR' group; -NRSOR' group; -NRSO₂R' group; -CSR group; -CS2R group; -NRCSR' group; -SCOR group; unsubstituted or substituted phenyl having one to three of the same or different halo, cyano, nitro, hydroxy (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH₂ group, NHZ group or NZZ' group; phenoxy where the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH₂ group, NHZ group or NZZ' group; phenylthio where the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alky, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) -

alkanoyloxy, NH₂ group, NHZ group or NZZ' group; or when two adjacent positions on the phenyl ring are substituted with alkoxy groups, these groups may be joined to form, together with the carbon atoms to which they are attached, a 5 or 6 membered dioxolano or dioxano heterocyclic ring;

where R, R' and R" are hydrogen or (C_1-C_6) - alkyl; Z and Z' are (C_1-C_4) alkyl and "amino" means NRR'; and

agronomically acceptable salts thereof.

The compositions of the invention also contain agronomically acceptable diluent or carrier.

The term "halo" should be understood as including chloro, fluoro, bromo and iodo. The term "alkyl" by itself or as a part of another substituent, unless otherwise stated, includes straight or branched chain groups such as methyl, ethyl, n-propyl, isopropyl, \underline{n} -butyl, \underline{t} -butyl, isobutyl and neopentyl and where indicated higher homologues and isomers such as \underline{n} -octyl and isooctyl. The term "haloalkyl" by itself or as part of another substituent is an alkyl group of the stated number of carbon atoms having one or more halo atoms bonded thereto such as chloromethyl, 1- or 2-bromoethyl and trifluoromethyl. Analogously, "cyanoalkyl" by itself or as part of another group is an alkyl group of the stated number of carbon atoms having one or more cyano groups bonded thereto; "haloalkoxy" by itself or as part of another group is an alkoxy group of the stated number of carbon atoms having one or more halo atoms bonded thereto such as difluoromethoxy, trifluoromethoxy, 2-fluoroethoxy and 2,2,2-trifluoroethoxy. "Alkenyl" and "alkynyl" by themselves or as part of another substituent comprise

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straight and branched chain groups of the stated number of carbon atoms. "Alkadienyl" is a straight or branched chain alkenyl group comprising two carbon-carbon double bonds that can be conjugated such as 1,3-butadienyl, cumulated such as 1,2-propadienyl or isolated such as 1,4-pentadienyl.

Specially interesting compounds, within the scope of the present invention include: N'-t-butyl-N-acetyl-N'-benzoylhydrazine N'-t-butyl-N-propionyl-N'-benzoylhydrazine N'-t-butyl-N-butyryl-N'-benzoylhydrazine N'-t-butyl-N-valeryl-N'-benzoylhydrazine N'-t-butyl-N-hexanoyl-N'-benzoylhydrazine N'-t-butyl-N-heptanoyl-N'-benzoylhydrazine N'-t-butyl-N-octanoyl-N'-benzoylhydrazine N'-t-butyl-N-nonanoyl-N'-benzoylhydrazine N'-t-butyl-N-decanoyl-N'-benzoylhydrazine N'-t-butyl-N-undecanoyl-N'-benzoylhydrazine N'-t-butyl-N-cyclopropylcarbonyl-N'-benzoylhydrazine N'-t-butyl-N-cyclobutylcarbonyl-N'-benzoylhydrazine $\verb|N'-\underline{t}-butyl-N-cyclohexylcarbonyl-N'-benzoylhydrazine|$ $N'-\underline{t}$ -butyl-N-cycloheptylcarbonyl-N'-benzoylhydrazine ${\tt N'-\underline{t}-butyl-N-cyclooctylcarbonyl-N'-benzoylhydrazine}$ N'-t-butyl-N-acryloyl-N'-benzoylhydrazine N'-t-butyl-N-allylcarbonyl-N'-benzoylhydrazine N'-t-butyl-N-(1-propenylcarbonyl)-N'-benzoylhydrazine N'-t-butyl-N-crotonoyl-N'-benzoylhydrazine N'-t-butyl-N-isocrotonyl-N'-benzoylhydrazine N'-t-butyl-N-cyclopropenylcarbonyl-N'-benzoylhydrazine N'-t-butyl-N-cyclobutenylcarbonyl-N'-benzoylhydrazine N'-t-butyl-N-cyclopentylcarbonyl-N'-benzoylhydrazine N'-t-butyl-N-cyclohexenylcarbonyl-N'-benzoylhydrazine N'-t-butyl-N-cycloheptenylcarbonyl-N'-benzoylhydrazine N'-<u>t</u>-butyl-N-cyclooctenylcarbonyl-N'-benzoylhydrazine N'-t-butyl-N-propioloyl-N'-benzoylhydrazine

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N'-t-butyl-N-(1-butynylcarbonyl)-N'-benzoylhydrazine
N'-\underline{t}-butyl-N-(l-pentynylcarbonyl)-N'-benzoylhydrazine
N'-t-butyl-N-(1-hexynylcarbonyl)-N'-benzoylhydrazine
N'-\underline{t}-butyl-N-(1-heptynylcarbonyl)-N'-benzoylhydrazine
N'-\underline{t}-butyl-N-(1-octynylcarbonyl)-N'-benzoylhydrazine
N'-t-butyl-N-(2-butynylcarbonyl)-N'-benzoylhydrazine
N'-t-butyl-N-(2-pentynylcarbonyl)-N'-benzoylhydrazine
N'-t-butyl-N-(3-methyl-1-butynylcarbonyl)-N'-benzoyl-
      hydrazine
N'-\underline{t}-butyl-N-(2-hexynylcarbonyl)-N'-benzoylhydrazine
N'-t-butyl-N-(3-hexynylcarbonyl)-N'-benzoylhydrazine
N'-\underline{t}-butyl-N-(3,3-dimethyl-1-butynylcarbonyl)-n'-
      benzoylhydrazine
N'-t-butyl-N-(4-octynylcarbonyl)-N'-benzoylhydrazine
N'-\underline{t}-butyl-N-benzylcarbonyl-N'-benzoylhydrazine
N'-\underline{t}-butyl-N-phenethylcarbonyl-N'-benzoylhydrazine
N'-t-butyl-N-(3-phenylpropylcarbonyl)-N'-benzoyl-
      hydrazine
 N'-t-butyl-N-(4-phenylbutylcarbonyl)-N'-benzoyl-
 N'-\underline{t}-butyl-N-(4-(4-chlorophenyl)butylcarbonyl)-N'-
       benzoylhydrazine
 N'-t-butyl-N-acetyl-N'-(4-chlorobenzoyl) hydrazine
 N'-\underline{t}-butyl-N-propionyl-N'-(4-chlorobenzoyl) hydrazine
 N'-\underline{t}-butyl-N-butyryl-N'-(4-chlorobenzoyl) hydrazine
 N'-\underline{t}-butyl-N-valeryl-N'-(4-chlorobenzoyl) hydrazine
 N'-\underline{t}-butyl-N-hexanoyl-N'-(4-chlerobenzoyl) hydrazine
 N'-t-butyl-N-heptanoyl-N'-(4-chlorobenzoyl)hydrazine
 N'-\underline{t}-butyl-N-octanoyl-N'-(4-chlorobenzoyl) hydrazine
 N'-t-butyl-N-nonanoyl-N'-(4-chlorobenzoyl)hydrazine
 N'-t-butyl-N-decancyl-N'-(4-chlorobenzoyl)hydrazinc
 N'-\underline{t}-butyl-N-undecanoyl-N'-(4-chlorobenzoyl)hydrazine
 N'-t-butyl-N-cyclopropylcarbonyl-N'-(4-chlorobenzoyl)-
       hydrazine
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N'-\underline{t}-butyl-N-cyclobutylcarbonyl-N'-(4-chlorobenzoyl)-hydrazine
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- $N'-\underline{t}$ -butyl-N-cyclohexylcarbonyl-N'-(4-chlorobenzoyl)-hydrazine
- $N'-\underline{t}$ -butyl-N-cycloheptylcarbonyl-N'-(4-chlorobenzoyl)-hydrazine
- N'-t-butyl-N-cyclooctylcarbonyl-N'-(4-chlorobenzoyl)-hydrazine
- N'-<u>t</u>-butyl-N-acryloyl-N'-(4-chlorobenzoyl)hydrazine
- N'-<u>t</u>-butyl-N-allylcarbonyl-N'-(4-chlorobenzoyl)hydrazine
- N'-t-butyl-N-(1-propenylcarbonyl)-N'-(4-chlorobenzoyl)-hydrazine
- N'-t-butyl-N-crotonoyl-N'-(4-chlorobenzoyl)hydrazine
- N'-t-butyl-N-isocrotonoyl-N'-(4-chlorobenzoyl)hydrazine
- N'-t-butyl-N-cyclopropenylcarbonyl-N'-(4-chlorobenzoyl)hydrazine
- N'-t-butyl-N-cyclobutenylcarbonyl-N'-(4-chlorobenzoyl)hydrazine
- $N'-\underline{t}$ -butyl-N-cyclopentylcarbonyl-N'-(4-chlorobenzoyl)-hydrazine
- $N'-\underline{t}$ -butyl-N-cyclohexenylcarbonyl-N'-(4-chlorobenzoyl)-hydrazine
- N'-<u>t</u>-butyl-N-cycloheptenylcarbonyl-N'-(4-chlorobenzoyl)hydrazine
- N'-t-butyl-N-cyclooctenylcarbonyl-N'-(4-chlorobenzoyl)-hydrazine
- $N'-\underline{t}$ -butyl-N-propioloyl-N'-(4-chlorobenzoyl)hydrazine
- $N'-\underline{t}$ -butyl-N-(1-butynylcarbonyl)-N'-(4-chlorobenzoyl)-hydrazine
- N'-t-butyl-N-(1-pentynylcarbonyl)-N'-(4-chlorobenzoyl)-hydrazine
- N'-<u>t</u>-butyl-N-(1-hexynylcarbonyl)-N'-(4-chlorobenzoyl)hydrazine

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N'-t-butyl-N-(1-heptynylcarbonyl)-N'-(4-chlorobenzoyl)-
              hydrazine
         N'-t-butyl-N-(1-octynylcarbonyl)-N'-(4-chlorobenzoyl)-
              hydrazine
         N'-t-butyl-N-(2-butynylcarbonyl)-N'-(4-chlorobenzoyl)-
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               hydrazine
         N'-t-butyl-N-(2-pentynylcarbonyl)-N'-(4-chlorobenzoyl)-
               hydrazine
         N'-t-butyl-N-(3-methyl-1-butynylcarbonyl)-N'-(4-chloro-
               benzoyl) hydrazine
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        . N'-t-butyl-N-(2-hexynylcarbonyl)-N'-(4-chlorobenzoyl)-
               hydrazine
          N'-t-butyl-N-(3-hexynylcarbonyl)-N'-(4-chlorobenzoyl)-
               hydrazine
          N'-\underline{t}-butyl-N-(3,3-dimethyl-l-butynylcarbonyl)-N'-(4-
15 '
                chlorobenzoyl) hydrazine
          N'-t-butyl-N-(4-octynylcarbonyl)-N'-(4-chlorobenzoyl)-
                hydrazine
          N'-t-butyl-N-benzylcarbonyl-N'-(4-chlorobenzoyl)-
                hydrazine
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          N'-t-butyl-N-phenethylcarbonyl-N'-(4-chlorobenzoyl)-
                hydrazine
          N'-t-butyl-N-(3-phenylpropylcarbonyl)-N'-(4-chloro-
                benzoyl) hydrazine
           N'-t-butyl-N-(4-phenylbutylcarbonyl)-N'-(4-chloro-
 25
                benzoyl)hydrazine
           N'-t-butyl-N-(4-(4-chlorophenyl)butylcarbonyl)-N'-(4-
                chlorobenzoyl)hydrazine
           N'-t-butyl-N-acetyl-N'-(3-toluoyl)hydrazine
           N'-t-butyl-N-propionyl-N'-(3-toluoyl)hydrazine
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           N'-t-butyl-N-butyryl-N'-(3-toluoyl)hydrazine
           N'-\underline{t}-butyl-N-valeryl-N'-(3-toluoyl)hydrazine
            N'-\underline{t}-butyl-N-hexanoyl-N'-(3-toluoyl) hydrazine
            N'-t-butyl-N-heptanoyl-N'-(3-toluoyl)hydrazine
            N'-\underline{t}-butyl-N-octanoyl-N'-(3-toluoyl)hydrazine
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N'-\underline{t}-butyl-N-nonanoyl-N'-(3-toluoyl) hydrazine
             N'-\underline{t}-butyl-N-decanoyl-N'-(3-toluoyl) hydrazine
             N'-\underline{t}-butyl-N-undecanoyl-N'-(3-toluoyl)hydrazine
             N'-\underline{t}-butyl-N-cyclopropylcarbonyl-N'-(3-toluoyl)-
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                   hydrazine
            N'-\underline{t}-butyl-N-cyclobutylcarbonyl-N'-(3-toluoyl)-
                   hydrazine
            N'-\underline{t}-butyl-N-cyclohexylcarbonyl-N'-(3-toluoyl)-
                   hydrazine
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            N'-\underline{t}-butyl-N-cycloheptylcarbonyl-N'-(3-toluoyl)-
                   hydrazine
            N'-\underline{t}-butyl-N-cyclooctylcarbonyl-N'-(3-toluoyl)-
                   hydrazine
            N'-\underline{t}-butyl-N-acryloyl-N'-(3-toluoyl) hydrazine
            N'-\underline{t}-butyl-N-allylcarbonyl-N'-(3-toluoyl)hydrazine
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            N'-\underline{t}-butyl-N-(1-propenylcarbonyl)-N'-(3-toluoyl)-
                   hydrazine
            N'-\underline{t}-butyl-N-crotonoyl-N'-(3-toluoyl) hydrazine
            N'-\underline{t}-butyl-N-isocrotonoyl-N'-(3-toluoyl) hydrazine
            N'-\underline{t}-butyl-N-cyclopropenylcarbonyl-N'-(3-toluoyl)-
 20
                  hydrazine.
            N'-\underline{t}-butyl-N-cyclobutenylcarbonyl-N'-(3-toluoyl)-
                  hydrazine
            N'-<u>t</u>-butyl-N-cyclopentylcarbonyl-N'-(3-toluoyl)-
25
                  hydrazine
            N'-\underline{t}-butyl-N-cyclohexenylcarbonyl-N'-(3-toluoyl)-
                  hydrazine
            N'-\underline{t}-butyl-N-cycloheptenylcarbonyl-N'-(3-toluoyl)-
                  hydrazine
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            N'-\underline{t}-butyl-N-cyclooctenylcarbonyl-N'-(3-toluoyl)-
                  hydrazine
            N'-\underline{t}-butyl-N-propioloyl-N'-(3-toluoyl)hydrazine
            N'-\underline{t}-butyl-N-(1-butynylcarbonyl)-N'-(3-toluoyl)-
                  hydrazine
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N'-\underline{t}-butyl-N-(1-pentynylcarbonyl)-N'-(3-toluoyl)-
               hydrazine
         N'-\underline{t}-butyl-N-(1-hexynylcarbonyl)-N'-(3-toluoyl)-
               hydrazine
         N'-t-butyl-N-(1-heptynylcarbonyl)-N'-(3-toluoyl)-
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               hydrazine
         N'-t-butyl-N-(1-octynylcarbonyl)-N'-(3-toluoyl)-
               hydrazine
         N'-\underline{t}-butyl-N-(2-butynylcarbonyl)-N'-(3-toluoyl)-
                hydrazine
10
         N'-t-butyl-N-(2-pentynylcarbonyl)-N'-(3-toluoyl)-
                hydrazine
          N'-t-butyl-N-(3-methyl-1-butynylcarbonyl)-N'-
                (3-toluoy1) hydrazine
          N'-\underline{t}-butyl-N-(2-hexynylcarbonyl)-N'-(3-toluoyl)-
15
                hydrazine
          N'-t-butyl-N-(3-hexynylcarbonyl)-N'-(3-toluoyl)-
                hydrazine
          N'-\underline{t}-butyl-N-(3,3-dimethyl-1-butynylcarbonyl)-N'-
                 (3-toluoy1) hydrazine
 20
          N'-t-butyl-N-(4-octynylcarbonyl)-N'-(3-toluoyl)-
                hydrazine
           N'-\underline{t}-butyl-N-benzylcarbonyl-N'-(3-toluoyl)hydrazine
           N'-\underline{t}-butyl-N-phenethylcarbonyl-N'-(3-toluoyl)-
                 hydrazine
 25
           N'-t-butyl-N-(3-phenylpropylcarbonyl)-N'-(3-toluoyl)-
                 hydrazine
           N'-\underline{t}-butyl-N-(4-phenylbutylcarbonyl)-N'-(3-toluoyl)-
                 hydrazine
           N'-t-butyl-N-(4-(4-chlorophenyl)butylcarbonyl)-N'-
 30
                 (3-toluoy1) hydrazine
           N'-t-butyl-N-acetyl-N'-(2-methoxybenzoyl)hydrazine
           N'-t-butyl-N-propionyl-N'-(2-methoxybenzoyl)hydrazine
           N'-\underline{t}-butyl-N-butyryl-N'-(2-methoxybenzoyl) hydrazine
            N'-\underline{t}-butyl-N-valeryl-N'-(2-methoxybenzoyl)hydrazine
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N'-\underline{t}-butyl-N-hexanoyl-N'-(2-methoxybenzoyl)hydrazine
          N'-\underline{t}-butyl-N-heptanoyl-N'-(2-methoxybenzoyl)hydrazine
          N'-t-butyl-N-octanoyl-N'-(2-methoxybenzoyl)hydrazine
          N'-\underline{t}-butyl-N-nonanoyl-N'-(2-methoxybenzoyl)hydrazine
5
          N'-\underline{t}-butyl-N-decanoyl-N'-(2-methoxybenzoyl) hydrazine
          N'-t-butyl-N-undecanoyl-N'-(2-methoxybenzoyl) hydrazine
          N'-\underline{t}-butyl-N-cyclopropylcarbonyl-N'-(2-methoxybenzoyl)-
                hydrazine
          N'-\underline{t}-butyl-N-cyclobutylcarbonyl-N'-(2-methoxybenzoyl)-
10
                hydrazine
          N'-\underline{t}-butyl-N-cyclohexylcarbonyl-N'-(2-methoxybenzoyl)-
                hydrazine
          N'-\underline{t}-butyl-N-cycloheptylcarbonyl-N'-(2-methoxybenzoyl)-
                hydrazine
15
          N'-\underline{t}-butyl-N-cyclooctylcarbonyl-N'-(2-methoxybenzoyl)-
                hydrazine
          N'-\underline{t}-butyl-N-acryloyl-N'-(2-methoxybenzoyl)hydrazine
          N'-\underline{t}-butyl-N-allylcarbonyl-N'-(2-methoxybenzoyl)-
                hydrazine
          N'-\underline{t}-butyl-N-(1-propenylcarbonyl)-N'-(2-methoxy-
20
                benzoyl) hydrazine
          N'-\underline{t}-butyl-N-crotonoyl-N'-(2-methoxybenzoyl)hydrazine
          N'-<u>t</u>-butyl-N-isocrotonoyl-N'-(2-methoxybenzoyl)-
                hydrazine
25
          N'-\underline{t}-butyl-N-cyclopropenylcarbonyl-N'-(2-methoxy-
                benzoyl) hydrazine
          N'-\underline{t}-butyl-N-cyclobutenylcarbonyl-N'-(2-methoxy-
                benzoyl) hydrazine
          N'-\underline{t}-butyl-N-cyclopentylcarbonyl-N'-(2-methoxybenzoyl)-
30
                hydrazine
          N'-\underline{t}-butyl-N-cyclohexenylcarbonyl-N'-(2-methoxy-
                  benzoyl) hydrazine
          N'-t-butyl-N-cycloheptenylcarbonyl-N'-(2-methoxy-
                benzoyl)hydrazine
35
          N'-\underline{t}-butyl-N-cyclooctenylcarbonyl-N'-(2-methoxy-
                benzoyl) hydrazine
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N'-t-butyl-N-propioloyl-N'-(2-methoxybenzoyl)hydrazine
N'-t-butyl-N-(1-butynylcarbonyl)-N'-(2-methoxybenzoyl)-
      hydrazine
N'-\underline{t}-butyl-N-(1-pentynylcarbonyl)-N'-(2-methoxy-
      benzoyl) hydrazine
N'-t-butyl-N-(1-hexynylcarbonyl)-N'-(2-methoxybenzoyl)-
      hydrazine
N'-t-butyl-N-(1-heptynylcarbonyl)-N'-(2-methoxy-
      benzoyl) hydrazine
N'-t-butyl-N-(1-octynylcarbonyl)-N'-(2-methoxybenzoyl)-
      hydrazine
N'-\underline{t}-butyl-N-(2-butynylcarbonyl)-N'-(2-methoxybenzoyl)-
      hydrazine
N'-t-butyl-N-(2-pentynylcarbonyl)-N'-(2-methoxy-
      benzoyl) hydrazine
N'-t-butyl-N-(3-methyl-1-butynylcarbonyl)-N'-(2-
      methoxybenzoyl) hydrazine
N'-\underline{t}-butyl-N-(2-hexynylcarbonyl)-N'-(2-methoxybenzoyl)-
      hydrazine
N'-t-butyl-N-(3-hexynylcarbonyl)-N'-(2-methoxybenzoyl)-
      hydrazine
N'-\underline{t}-butyl-N-(3,3-dimethyl-1-butynylcarbonyl)-N'-(2-
      methoxybenzoyl)hydrazine
N'-\underline{t}-butyl-N-(4-octynylcarbonyl)-N'-(2-methoxybenzoyl)-
      hydrazine
 N'-\underline{t}-butyl-N-benzylcarbonyl-N'-(2-methoxybenzoyl)-
      hydrazine
 N'-\underline{t}-butyl-N-phenethylcarbonyl-N'-(2-methoxybenzoyl)-
      hydrazine
 N'-\underline{t}-butyl-N-(3-phenylpropylcarbonyl)-N'-(2-methoxy-
      benzoyl) hydrazine
 N'-t-butyl-N-(4-phenylbutylcarbonyl)-N'-(2-methoxy-
       benzoyl)hydrazine
 N'-\underline{t}-butyl-N-(4-(4-chlorophenyl)butylcarbonyl)-N'-(2-
       methoxybenzoyl)hydrazine
 N'-\underline{t}-butyl-N-acetyl-N'-(3-fluorobenzoyl)hydrazine
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N'-\underline{t}-butyl-N-propionyl-N'-(3-fluorobenzoyl) hydrazine
 N'-\underline{t}-butyl-N-butyryl-N'-(3-fluorobenzoyl)hydrazine
 N'-t-butyl-N-valeryl-N'-(3-fluorobenzoyl)hydrazine
 N'-\underline{t}-butyl-N-hexanoyl-N'-(3-fluorobenzoyl) hydrazine
N'-\underline{t}-butyl-N-heptanoyl-N'-(3-fluorobenzoyl) hydrazine
N'-\underline{t}-butyl-N-octanoyl-N'-(3-fluorobenzoyl) hydrazine
N'-\underline{t}-butyl-N-nonanoyl-N'-(3-fluorobenzoyl) hydrazine
N'-t-butyl-N-decanoyl-N'-(3-fluorobenzoyl)hydrazine
N'-\underline{t}-butyl-N-undecanoyl-N'-(3-fluorobenzoyl) hydrazine
N'-t-butyl-N-cyclopropylcarbonyl-N'-(3-fluorobenzoyl)-
      hydrazine
N'-t-butyl-N-cyclobutylcarbonyl-N'-(3-fluorobenzoyl)-
      hydrazine
N'-t-butyl-N-cyclohexylcarbonyl-N'-(3-fluorobenzoyl)-
      hydrazine
N'-t-butyl-N-cycloheptylcarbonyl-N'-(3-fluorobenzoyl)-
     hydrazine
N'-\underline{t}-butyl-N-cyclooctylcarbonyl-N'-(3-fluorobenzoyl)-
      hydrazine
N'-\underline{t}-butyl-N-acryloyl-N'-(3-fluorobenzoyl)hydrazine
N'-\underline{t}-butyl-N-allylcarbonyl-N'-(3-fluorobenzoyl)-
      hydrazine
N'-t-butyl-N-(1-propenylcarbonyl)-N'-(3-fluorobenzoyl)-
     hydrazine
N'-t-butyl-N-crotonoyl-N'-(3-fluorobenzoyl)hydrazine
N'-t-butyl-N-isocrotonoyl-N'-(3-fluorobenzoyl)hydrazine
N'-\underline{t}-butyl-N-cyclopropenylcarbonyl-N'-(3-fluoro-
     benzoyl)hydrazine
N'-\underline{t}-butyl-N-cyclobutenylcarbonyl-N'-(3-fluorobenzoyl)-
     hydrazine
N'-t-butyl-N-cyclopentylcarbonyl-N'-(3-fluorobenzoyl)-
     hydrazine
N'-\underline{t}-butyl-N-cyclohexenylcarbonyl-N'-(3-fluorobenzoyl)-
     hydrazine
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N'-t-butyl-N-cycloheptenylcarbonyl-N'-(3-fluoro-
               benzoyl)hydrazine
         N'-t-butyl-N-cyclooctenylcarbonyl-N'-(3-fluorobenzoyl)-
               hydrazine
         N'-t-butyl-N-propioloyl-N'-(3-fluorobenzoyl)hydrazine
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         N'-t-butyl-N-(1-butynylcarbonyl)-N'-(3-fluorobenzoyl)-
               hydrazine
         N'-t-butyl-N-(1-pentynylcarbonyl)-N'-(3-fluorobenzoyl)-
               hydrazine
         N'-t-butyl-N-(1-hexynylcarbonyl)-N'-(3-fluorobenzoyl)-
10
               hydrazine
         N'-t-butyl-N-(1-heptynylcarbonyl)-N'-(3-fluorobenzoyl)-
               hydrazine
         N'-t-butyl-N-(1-octynylcarbonyl)-N'-(3-fluorobenzoyl)-
               hydrazine.
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          N'-t-butyl-N-(2-butynylcarbonyl)-N'-(3-fluorobenzoyl)-
               hydrazine ·
         N'-t-butyl-N-(2-pentynylcarbonyl)-N'-(3-fluorobenzoyl)-
               hydrazine
          N'-t-butyl-N-(3-methyl-1-butynylcarbonyl)-N'-(3-fluoro-
20
               benzoyl)hydrazine
          N'-\underline{t}-butyl-N-(2-hexynylcarbonyl)-N'-(3-fluorobenzoyl)-
               hydrazine
          N'-t-butyl-N-(3-hexynylcarbonyl)-N'-(3-fluorobenzoyl)-
25
               hydrazine
          N'-\underline{t}-butyl-N-(3,3-dimethyl-1-butynylcarbonyl)-N'-(3-
               fluorobenzoyl) hydrazine
          N'-\underline{t}-butyl-N-(4-octynylcarbonyl)-N'-(3-fluorobenzoyl)-
               hydrazine
          N'-\underline{t}-butyl-N-benzylcarbonyl-N'-(3-fluorobenzoyl)-
30
               hydrazine '
          N'-\underline{t}-butyl-N-phenethylcarbonyl-N'-(3-fluorobenzoyl)-
               hydrazine
          N'-\underline{t}-butyl-N-(3-phenylpropylcarbonyl)-N'-(3-fluoro-
                benzoyl)hydrazine
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- $N'-\underline{t}$ -butyl-N-(4-phenylbutylcarbonyl)-N'-(3-fluoro-benzoyl)hydrazine
- N'-t-butyl-N-(4-(4-chlorophenyl)butylcarbonyl)-N'-(3-fluorobenzoyl)hydrazine

Because of their good insecticidal activity, preferred compounds of the present invention for use in the insecticidal compositions and formulations include those where, any one or any combination of two or more of the substituents conforms to the following definitions:

X and X' are O or S;

- R^1 is unsubstituted (C_3-C_8) branched alkyl or (C_1-C_4) straight chain alkyl substituted with one or two of the same or different (C_3-C_4) cycloalkyl;
- A is unsubstituted or substituted (C₁-C₆)alkyl having one to three of the same or different halo, cyano, nitro, (C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)-alkanoyloxy, NH₂, NHZ or NZZ';

(C₃-C₆) cycloalkyl;

 (C_2-C_6) unsubstituted or substituted alkenyl having one to three of the same or different halo, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, (C_1-C_4) alkoxy or halo (C_1-C_4) alkoxy;

(C3-C6) cycloalkenyl; or

phenalkyl having one or two carbon atoms in the alkyl group and the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, nitro or (C_1-C_4) alkyl;

B is unsubstituted naphthyl; or

unsubstituted or substituted phenyl where the substituents can be from one to three of the same or different halo; nitro; cyano; (C_1-C_4) alkyl; halo (C_1-C_4) alkyl; cyano $(C_1 - C_4)$ alkyl; $(C_1 - C_4)$ alkoxyl; alkoxyalkyl having independently 1 to 4 carbon atoms in each alkyl group; -COD4 group; carboxy; (C₁-C₄)alkoxy-carbonyl; (C₁-C₄)alkanoyloxy; -ND⁴D⁵ group; (C₁-C₄)alkyl- thio; -CSD⁴ group; -CS₂D⁴ group; -SCOD group; unsubstituted or substituted phenyl having one to two of the same or different halo, nitro, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, NH₂, NHZ or NZZ'; phenoxy where the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, nitro, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, $(C_1 - C_4)$ - alkoxy-carbonyl, $(C_1 - C_4)$ alkanoyloxy, NH2, NHZ or NZZ'; or when two adjacent positions on the phenyl ring are substituted with alkoxy groups, these groups may be joined to form, together with the carbon atoms to which they are attached, a 5- or 6-membered dioxolano or dioxano heterocyclic ring;

where D^4 and D^5 are hydrogen or (C_1-C_4) alkyl; Z and Z' are (C_1-C_4) alkyl; and agronomically acceptable salts.

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Insecticidal compounds of the present invention having very good activity for use in the insecticidal compositions and formulations of the present invention include those where, any one or any combination of two or more of the substituents conforms to the following definitions:

X and X' are O or S; R¹ is branched (C₃-C₈)alkyl;

A is unsubstituted or substituted (C₁-C₆)alkyl having one to three of the same or different halo, cyano, nitro, carboxy or (C₁-C₄)alkoxy-carbonyl;

cyclohexyl;

unsubstituted or substituted (C_2-C_6) alkenyl having one to three of the same of different halo or (C_1-C_4) alkyl;

cyclohexenyl; or

benzyl where the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, methyl or ethyl;

B is unsubstituted naphthyl; or

unsubstituted or substituted phenyl having one to three of the same or different halo; nitro; cyano; (C_1-C_4) alkyl; halo (C_1-C_4) alkyl; cyano (C_1-C_4) alkyl; (C_1-C_4) alkoxy; $-COD^4$ group; (C_1-C_4) alkoxy-carbonyl; (C_1-C_4) alkanoyloxy; or unsubstituted or substituted phenyl having one or two of the

same or different halo, nitro, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH₂, NHZ or NZZ'; where D⁴ is hydrogen or (C_1-C_4) alkyl; Z and Z' are (C_1-C_4) alkyl; and

agronomically acceptable salts thereof.

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Because of their excellent insecticidal activity, most preferred compounds of the present invention for use in the insecticidal compositions and formulations of the present invention include those where any one or combination of two or more of the substituents coform to the following definitions:

X and X' are 0;
R¹ is branched (C₄-C₇)alkyl;

A is (C₁-C₆) unsubstituted or substituted alkyl having one or two of the same or different halo;

cyclohexyl;

(C₂-C₆) unsubstituted or substituted alkenyl having one to three of the same or different halo, methyl or ethyl;

cyclohexenyl; or

benzyl;

B is unsubstituted or substituted phenyl where the substituents can be from one to three of the same or different halo, (C_1-C_4) - alkyl, (C_1-C_4) alkoxy or (C_1-C_4) haloalkyl; and

agronomically acceptable salts thereof.

Because of their outstanding insecticidal activity, most particularly preferred compounds of the present invention for use in the insecticidal compositions and formulations of the present invention include those where any one or combination of two or more of the substituents conform to the following definitions:

X and X' are 0;
R¹ is t-butyl, neopentyl (2,2-dimethylpropyl) or
 1,2,2-trimethylpropyl;
A is (C₃-C₅) unsubstituted alkyl;

cyclohexyl;

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(C₂-C₄)alkenyl unsubstituted or substituted with one to three of the same or different chloro, bromo or methyl;

cyclohexenyl; or

benzyl;

B is unsubstituted or substituted phenyl where the substituents can be one or two of the same or different chloro, fluoro, bromo, iodo, methyl, ethyl, methoxy or trifluoromethyl; and

agronomically acceptable salts thereof.

Those N'-substituted-N-alkylcarbonyl-N'-acyl hydrazines of the invention which possess acidic or basic functional groups may be further reacted to form novel salts with appropriate bases or acids. These salts also exhibit insecticidal activity. Typical salts are the agronomically acceptable metal salts, ammonium salts and acid addition salts. Among the

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metal salts are those in which the metal cation is an alkali metal cation such as sodium, potassium or lithium; alkaline earth metal cation such as calcium, magnesium, barium or strontium; or heavy metal cation such as zinc, manganese, cupric, cuprous, ferric, ferrous, titanium or aluminum. The ammonium salts include those in which the ammonium cation has the formula $NR^5R^6R^7R^8$ wherein each of R^5 , R^6 , R^7 and R^8 is independently hydrogen, hydroxy, (C1-C4) alkoxy, (C_1-C_{20}) alkyl, (C_3-C_8) alkenyl, (C_3-C_8) alkynyl, (C_2-C_8) hydroxyalkyl, (C2-C3) alkoxyalkyl, (C2-C6) aminoalkyl, (C2-C6) haloalkyl, NH2, NHZ or NZZ'; substituted or unsubstituted phenyl, substituted or unsubstituted phenylalkyl, having up to four carbon atoms in the alkyl moiety, or any two of R⁵, R⁶, R⁷ or R⁸ can be taken to form together with the nitrogen atom, a 5- or 6-membered heterocyclic ring, optionally having up to one additional hetero atom (e.g., oxygen, nitrogen, or sulfur) in the ring, and preferably saturated, such as piperidino, morpholino, pyrrolidino, piperazino or the like, or any three of R^5 , R^6 , R^7 or R^8 can be taken to form together with the nitrogen atom, a 5- or 6-membered aromatic heterocyclic ring, such as piperazole or pyridine. When R^5 , R^6 , R^7 or R^8 substituent in the ammonium group is as substituted phenyl or substituted phenylalkyl, the substituents on the phenyl and phenalkyl will generally be selected from halo, (C_1-C_8) alkyl, (C_1-C_4) alkoxy, hydroxy, nitro, trifluoromethyl, cyano, amino and (C1-C4) alkylthio. Such substituted phenyl groups preferably have up to two such substituents. Representative ammonium cations include ammonium, dimethylammonium, 2-ethylhexylammonium, bis(2-hydroxyethyl)ammonium, tris(2-hydroxyethyl)ammonium, dicyclohexylammonium, t-octylammonium, 2-hydroxyethylammonium, morpholinium, piperidinium,

2-phenethylammonium, 2-methylbenzylammonium, n-hexylammonium, triethylammonium, trimethylammonium, tri(n-butyl)-ammonium, methoxyethylammonium, diisopropylammonium, pyridinium, dialkylammonium, pyrazolium, propargylammonium, dimethylhydrazinium, octadecylammonium, 4-dichlorophenylammonium, 4-nitrobenzylammonium, benzyltrimethylammonium, 2-hydroxyethyldimethyloctadecylammonium, 2-hydroxyethyldiethyloctylammonium, decyltrimethylammonium, hexyltriethylammonium, 4-methylbenzyltrimethylammonium, and the like. Among the acid addition salts are those in which the anion is an agronomically acceptable anion such as hydrochloride, hydrobromide, sulfate, nitrate, perchlorate, acetate and oxalate.

The compounds of this invention or their precursors can be prepared according to the following processes. Process A can be used when preparing compounds according to Formula I where X and X' are both oxygen.

O <u>Process A:</u>

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Step 1

Step 2

where R^1 , A and B are as defined above for Formula I and X and X' are oxygen.

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Alternatively, process B can be used when preparing compounds according to Formula I where X and X' are oxygen, and R¹, A and R are as defined above for Formula I.

Process B: Step 1 VIII VII VI Step 2 Reducing Agent C-NHN=0 Catalyst (optional) (IV) IX VIII Step 3 NHNHCH X (I)

where X and X' are oxygen, A and B are as defined above for Formula I, and R^2 and R^3 are the same or different hydrogen or (C2-C9) straight or branched chain alkyl provided that R^2 and R^3 are not both H or R^2 or R^3 is not a straight chain alkyl group when the other $(R^2$ or R³) is hydrogen. As can be seen above, the

(IV)

IX

intermediate product of Step 2, the compounds of Formula IX, corresponds to the compounds of Formula IV. In addition, the compound of Formula X corresponds to the compounds of Formula I where X and X' are oxygen.

Process C can be used when preparing compounds according to Formula I where A, B and \mathbb{R}^1 are as defined for Formula I and at least one of X and X' is sulfur.

Process C: Step 1

wherein A, B and R¹ are as defined above for Formula I and at least one of X and X' is sulfur, and Y is a good leaving group such as carboxyalkylthio (for example, carboxymethylthio -SCH₂CO₂H); alkylthio (for example, methylthio); or halo (for example, chloro).

Process D can be used when preparing compounds according to Formula I where X and X' are oxygen and ${\sf R}^1$, A and B are as defined above for Formula I.

wherein A, B and R^1 are as defined above for Formula I and Z is \underline{t} -butyl; ethyl; phenyl; or benzyl.

Process E can be used when preparing compounds according to Formula I where X and X' are oxygen and \mathbb{R}^1 , A and B are as defined above for Formula I.

wherein R¹, A and B are as defined above for Formula I and W is hydrogen, methyl or ethyl; and W' is methyl, ethyl, phenyl or isobutyl.

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In process A, a compound of Formula II is reacted with a monosubstituted hydrazine of Formula III or a corresponding acid addition salt such as the



hydrochloride salt or the like, in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford an intermediate product of Formula IV which can be isolated or further reacted with a compound of Formula V in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford the desired product of Formula I.

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Examples of the compounds of Formula II which can be used in the above processes include cyclohexyl-carbonyl chloride, n-butanoyl chloride, n-pentanoyl chloride, phenylacetyl chloride, l-cyclohexenecarbonyl chloride, pivaloyl chloride, trichloroacetyl chloride, methacryloyl chloride and the like.

Examples of the compounds of Formula V which can be used in the above processes include benzoyl chloride, 4-chlorobenzoyl chloride, 4-methylbenzoyl chloride, 3,5-dichlorobenzoyl chloride, 2-bromobenzoyl chloride, 3-cyanobenzoyl chloride and the like.

The compounds of Formula II and/or Formula V are generally commercially available or can be prepared by known procedures.

Examples of the compounds of Formula III which can be used in the above processes include isopropylhydrazine, t-butylhydrazine, neopentylhydrazine, alpha-methylneopentylhydrazine, isobutylhydrazine, isopentylhydrazine, isooctylhydrazine, and the like. The compounds of Formula III are generally commercially available or can be prepared by known procedures.

Suitable solvents for use in the above processes include water; alcohols such as methanol, ethanol, isopropanol and the like; hydrocarbons such as toluene, xylene, hexane, heptane and the like; glyme; tetrahydrofuran; acetonitrile, pyridine; or haloalkanes such as methylene chloride or mixtures of these

solvents.

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Preferred solvents are water, toluene, methylene chloride or a mixture of these solvents.

Examples of bases for use in the above processes include tertiary amines such as triethylamine; pyridine; potassium carbonate; sodium carbonate; sodium bicarbonate; sodium hydroxide; or potassium hydroxide. Preferred bases are sodium hydroxide, potassium hydroxide or triethylamine.

In Process B, a compound of Formula VI is reacted with a ketone or aldehyde of Formula VII in an inert or substantially inert solvent or mixture of solvents and optionally in the presence of a catalyst to afford an intermediate product of Formula VIII. The intermediate product of Formula VIII is then further reacted with a reducing agent in an inert or substantially inert solvent or mixture of solvents to afford a second intermediate product of Formula IX (IV) which can be isolated or further reacted with a compound of Formula V in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford the desired product of Formula X (I).

Examples of the compounds of Formula VI which can be used in the above Process B include cyclohexane carboxylic acid hydrazide, n-butanoic acid hydrazide, n-pentanoic acid hydrazide, phenylacethydrazide, l-cyclohexene carboxylic acid hydrazide, pivalic acid hydrazide, trichloroacethydrazide, methacrylic acid hydrazide and the like. The compounds of Formula VI are generally commercially available or can be prepared by known procedures.

Examples of the compounds of Formula VII which can be used in the above Process B include 1,1,1-trimethylacetaldehyde, methylethylketone, diethylketone and the like. The compounds of Formula VII are

generally commercially available or can be prepared by known procedures.

Optionally, a catalyst may be used in Step 1 of Process B. Suitable catalysts generally include organic acids such as acetic acid, trifluoroacetic acid, oxalic acid and the like; mineral acids such as hydrochloric acid, sulfuric acid, nitric acid and the like; arylsulfonic acids such as toluenesulfonic acid; or pyridinium toluenesulfonate. Preferred catalysts are organic acids or arylsulfonic acids. Most preferred catalyst are acetic acid or trifluoroacetic acid.

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Suitable solvents for use in the above Process B, Step 1, include alcohols such as methanol, ethanol, isopropanol and the like; hydrocarbons such as toluene, benzene; ethers such as tetrahydrofuran (THF), glyme and the like; or dimethylformamide. Preferred solvents are alcohols and hydrocarbons. Most preferred solvents are alcohols such as methanol or ethanol.

Examples of suitable reducing agents for use in the above Process B, Step 2, include hydrides such as sodium borohydride and derivatives thereof such as sodium cyanoborohydride, lithium aluminum hydride and derivatives thereof and the like; or diborane. Preferred reducing agents are sodium borohydride and derivatives thereof or lithium aluminum hydride and derivatives thereof. Most preferred as a reducing agent is sodium cyanoborohydride.

Optionally, in Process B, Step 2, a catalyst may be included. Examples of suitable catalysts include organic acids such as acetic acid, trifluoroacetic acid; or mineral acids such as hydrochloric acid, sulfuric acid and the like. Preferred catalysts are organic acids or hydrochloric acid. Most preferred catalysts are acetic acid, trifluoroacetic acid or

hydrochloric acid.

Suitable solvents for use in the above Process B, Step 2, include alcohols such as methanol, ethanol, isopropanol and the like; ethers such as tetrahydrofuran (THF), diethylether, glyme and the like; or halohydrocarbons such as methylene chloride, chloroform and the like. Preferred solvents are alcohols and most preferred are methanol or ethanol.

Step 3 of Process B corresponds to Step 2 of Process A. Consequently, those bases and solvents suitable for use in Step 2 of Process A are suitable for use in Step 3 of Process B including the preferred bases and solvents described above.

In Process C, a compound of Formula XI is reacted with a monosubstituted hydrazine of Formula III or a corresponding acid addition salt such as the hydrochloride salt or the like in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford an intermediate compound of Formula XII which can be isolated or further reacted with a compound of Formula XIII in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford the desired product of Formula I.

Examples of the compounds of Formula XI which can be used in the above Process C include methylthio-thiobutyrate, methylthio-thiopentanoate, methylthio-thiocyclopentanecarboxylate, methylthio-alpha-phenylthioacetate and the like.

Examples of the compounds of Formula XIII which can be used in the above Process C include 3-methyl-methylthio-thiobenzoate, 4-chloromethylthio-thiobenzoate, benzoate, 4-methyl-methylthio-thiobenzoate, carboxy-methylthio-thiobenzoate and the like.

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The compounds of Formula XI and/or Formula XII are generally commercially available or can be prepared by known procedures.

Suitable solvents for use in the above Process C are generally polar high-boiling solvents such as dimethylformamide (DMF); glyme; tetrahydrofuran (THF); and pyridine. The preferred solvent is pyridine.

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Suitable bases for use in the above Process C include tertiary amines such as triethylamine; and pyridine. The preferred base is pyridine.

In Process D, a monosubstituted hydrazine of Formula III or a corresponding acid addition salt, such as the hydrochloride salt or the like, is reacted with a compound of Formula XIV in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford an intermediate product of Formula The intermediate product of Formula XV is then further reacted with a compound of Formula V in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford a second intermediate product of Formula XVI. The second intermediate product of Formula XVI is then further reacted with an acid in an inert or substantially inert solvent or mixture of solvents to afford a third intermediate product of Formula XVII. The third intermediate product of Formula XVII is then further reacted with a compound of Formula II in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford the desired product of Formula I.

Examples of the compounds of Formula XIV which can be used in the above Process D include di-t-butyl-carbonate, diethylcarbonate, diphenylcarbonate, dibenzylcarbonate and the like. The compounds of Formula XIV are generally commercially available or can

be prepared by known procedures.

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Suitable solvents for use in the above Process D, Steps 1, 2 and 4 include water; tetrahydrofuran; dioxane; toluene; alcohols such as methanol, ethanol and isopropanol; hexane; acetonitrile; pyridine; and haloalkanes such as methylene chloride; or mixtures of these solvents.

Preferred solvents are dioxane; toluene; tetrahydrofuran; pyridine; methylene chloride or water.

Most preferred solvents are dioxane; water or toluene.

Examples of the bases for use in the above Process D Steps 1, 2 and 4 include tertiary amines such as triethylamine; pyridine; potassium carbonate, sodium carbonate; sodium bicarbonate; sodium hydroxide; and potassium hydroxide.

Preferred bases are sodium hydroxide; potassium hydroxide; pyridine or triethylamine.

Suitable solvents for use in the above Process D, Step 3 include alcohols such as methanol, ethanol and isopropanol; water; tetrahydrofuran; dioxane; and acetonitrile.

Preferred solvents are methanol or ethanol.

Examples of acids for use in the above Process D, Step 3 include concentrated hydrochloric acid or concentrated sulfuric acid.

In Process E, a monosubstituted hydrazone of Formula III or a corresponding acid addition salt such as the hydrochloride salt or the like is reacted with a ketone or aldehyde of Formula XVIII in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford an intermediate product of Formula XIX. The intermediate product of Formula XIX is then further reacted with a compound of Formula V in the presence of a base in an inert or substantially

inert solvent or mixture of solvents to afford a second intermediate product of Formula XX. The second intermediate product of Formula XX is then further reacted with an acid in the presence of an inert or substantially inert solvent or mixture of solvents to afford a third intermediate product of Formula XVII. The third intermediate product of Formula XVII is then further reacted with a compound of Formula II in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford the desired product of Formula I.

Examples of the compounds of Formula XVIII which can be used in the above Process E include acetone, benzaldehyde, methyl ethyl ketone, acetophenone and isobutyraldehyde.

Preferably, acetone is used. The compounds of Formula XVIII are generally commercially available or can be prepared by known procedures.

Suitable solvents for use in the above Process E, Steps 1, 2 and 4 include alcohols such as methanol, ethanol, isopropanol and <u>n</u>-propanol; methylene chloride; toluene; tetrahydrofuran; acetontrile; water; ether; and pyridine.

Preferred solvents are alcohols such as methanol or ethanol; toluene; methylene chloride; water; tetrahydrofuran; or pyridine.

Most preferred solvent are methanol, ethanol, toluene, water or pyridine.

Examples of bases for use in the above Process E, Steps 1, 2 and 4 include triethylamine, potassium hydroxide, sodium hydroxide, potassium carbonate and pyridine.

preferred bases are sodium hydroxide or pyridine.

Suitable solvents for use in the above Process

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E, Step 3 include alcohols such as methanol, ethanol, isopropanol and \underline{n} -propanol; tetrahydrofuran; toluene; acetonitrile; water; and dioxane.

Preferred solvents are methanol, ethanol, tetrahydrofuran or water.

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Examples of acids for use in the above Process E, Step 3 include dilute hydrochloric acid or dilute sulfuric acid.

The above processes A and B can be carried out at temperatures between about -20°C and about 100°C. Preferably, these reactions are carried out between about -5°C and about 50°C.

Process C can be carried out at temperatures between about 10°C and 200°C. Preferably, this reaction is carried out between about 70°C and about 100°C.

Preparation of the compounds of the present invention by processes A, B and C is preferably carried out at about atmospheric pressure although higher or lower pressures can be used if desired.

Substantially equimolar amounts of reactants are preferably used in processes A, B and C although higher or lower amounts can be used if desired.

Generally, about one equivalent of base is used per equivalent of starting material of Formula II, V, XI and/or XIII. Where the acid addition salt of the monosubstituted hydrazine of Formula III is used, one additional equivalent of base is used. For example, in Process A, when substituents A and B are the same and a monosubstituted hydrazine is used, about two equivalents of base are used since about two equivalents of a suitably substituted benzoyl chloride of Formula II or V are employed. In Process A, when substituents A and B are different and an acid addition salt of the monosubstituted hydrazine of Formula III is used, about

two equivalents of base are used in step 1 and about one equivalent of base is used in step 2.

The above Processes D and E can be carried out at temperatures between about 0°C and about 100°C. Preferably, these reactions are carried out between about 0°C and about 50°C.

Preparation of the compounds of the present invention by Processes D and E is preferably carried out at about atmospheric pressure although higher or lower pressures can be used if desired.

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Substantially equimolar amounts of reactants are preferably used in Processes D and E although higher or lower amounts can be used if desired.

Generally, about one equivalent of base is used per equivalent of starting material or intermediate product in each of Steps 1, 2 and 4 of Processes D and E. Where the acid addition salt of the monosubstituted hydrazine of Formula III is used, one additional equivalent of base is used.

Modifications to the above processes may be necessary to accommodate reactive functionalities of particular A and/or B substituents. Such modifications would be apparent and known to those skilled in the art.

The agronomically acceptable salts embraced by Formula I of the invention can be prepared by reacting a metal hydroxide, a metal hydride or an amine or ammonium salt, such as a halide, hydroxide or alkoxide with a compound of Formula I having one or more hydroxy or carboxy groups or reacting a quaternary ammonium salt, such as chloride, bromide, nitrate or the like with a metal salt of a compound of Formula I in a suitable solvent. When metal hydroxides are used as reagents, useful solvents include water; ethers such as glyme and the like; dioxane; tetrahydrofuran; alcohols

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such as methanol, ethanol, isopropanol and the like. When metal hydrides are used as reagents, useful solvents include nonhydroxylic solvents, for example, ethers such as dioxane, glyme, diethylether and the like; tetrahydrofuran; hydrocarbons such as toluene, xylene, hexane, pentane, heptane, octane; dimethylformamide, and the like. When amines are used as reagents, useful solvents include alcohols, such as methanol or ethanol; hydrocarbons, such as toluene, xylene, hexane and the like; tetrahydrofuran; glyme; dioxane; or water. When ammonium salts are used as reagents, useful solvents include water; alcohols, such as methanol or ethanol; glyme; tetrahydrofuran; or the When the ammonium salt is other than a hydroxide or alkoxide, an additional base, such as potassium or sodium hydroxide, hydride, or alkoxide is generally The particular choice of solvent will depend on the relative solubilities of the starting materials and the resultant salts, and slurries rather than solutions of certain reagents may be used to obtain the salts. Generally, equivalent amounts of the starting reagents are used and the salt-forming reaction is carried out at about 0°C to about 100°C, preferably at about room temperature.

The acid addition salts of the present invention can be prepared by reacting hydrochloric, hydrobromic, sulfuric, nitric, phosphoric, acetic, propionic, benzoic or other suitable acid with a compound of Formula I having a basic functional group in a suitable solvent. Useful solvents include water, alcohols, ethers, esters, ketones, haloalkanes and the like. The particular choice of solvent will depend on the relative solubilities of the starting materials and the resulting salts and slurries rather than solutions of certain reagents may be used to obtain the salts.

Generally, equivalent molar amounts of starting materials are used and the salt-forming reaction is carried out at from about -10°C to about 100°C, preferably at about room temperature.

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The following Examples and the individual substituents mentioned therein and each and every combination of, or group containing, two or more of these substituents will further illustrate this invention but are not intended to limit it in any way. In Table I, some N'-substituted-N-alkylcarbonyl-N'-acyl-hydrazines of the present invention that have been made are listed. Structures were confirmed by NMR and in some cases by IR and/or elemental analysis. Specific illustrative preparation of the compounds of Examples 1, 3, 9, 11, 14 and 15 are described after Table I.

TABLE I

Ex.				R		
No.	<u>x</u>	<u>x '</u>	R ¹	A	В	m.p. °C
1	0	0	-C (CH ₃) 3	<u>s</u>	-C ₆ H ₅	>250
2	0	0	-C (CH ₃) ₃	-CH ₂ CH ₂ CH ₃	-C ₆ H ₄ Cl-4	177-179
3	0	0	-C (CH ₃) ₃	-CH ₂ CH ₂ CH ₂ CH ₃	-С ₆ н ₅	87-90
4	0	0	-C (CH ₃) ₃	-CH ₂ CH ₂ CH ₂ CH ₃	-C ₆ H ₄ Cl-4	179-180
5	0	0	-C (CH ₃) ₃	-сн ₂ сн ₂ сн ₂ сн ₃	-С ₆ н ₄ Сн ₃ -4	127-128
6	0	0	-C (CH ₃) ₃	-CH ₂ CH ₂ CH ₃	-с ₆ н ₅	114-115
7	0	0	-c (CH ₃) 3	-CH2CH2CH2CH3	-C ₆ H ₄ F-4	143-144
8	0	0	-с (сн ₃) 3	-сн ₂ сн ₂ сн ₂ сн ₃	-C ₆ H ₄ CF ₃ -4	195-196
9	0	0	-с (сн ³) ³	-СH ₂ С ₆ H ₅	-C ₆ H ₅	150-152
10	0	0	-C (CH ₃) ₃	-с (СH ₃) ₃	-C ₆ H ₄ C1-4	195-196
11	0	0	-с (сн ₃) 3	$\overline{\langle}$	-C ₆ H ₅	185-187
12	0	0	-C (CH ₃) 3	-CH ₂ C1	-C ₆ H ₅	172-173
13	0	0	-с (сн ₃) 3	-chc1 ₂	-c ₆ H ₅	192-193
14	0	0	-c (CH ₃) ₃	-cc1 ₃	-C ₆ H ₅	139-141
15	0	0	-C (CH ₃) ₃	-с (сн ₃) ₂ сн ₂ с1	-C ₆ H ₅	233-234
16	0	0	-C (CH ₃),	-c(c1)=cc1 ₂	-C ₆ H ₅	184-186
17	0	0	-C (CH ₃) ₃	-CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	-C ₆ H ₃ Cl ₂ -3,4	157-158
18	0	0	-с (сн ³) ³	-CII ₂ CH ₂ CH ₂ CH ₂ CH ₃	-C ₆ H ₄ CH ₃ -3	65-78
19	0	0	-C (CH ₃) ₃	$-C(CH_3)=CH_2$	-c ₆ H ₅	127-130
20	0	0	-c (cH ₃) ₃	$\dot{\Box}$	-C ₆ H ₅	

EXAMPLE NO. 1 - Preparation of N'-t-butyl-N-cyclohexyl-carbonyl-N'-benzoylhydrazine

To a stirred suspension of \underline{t} -butylhydrazine hydrochloride (2.0 g, 0.016 M) in toluene (30 ml) was added 50% sodium hydroxide (1.3 g, 0.016 M). After 15 minutes, the mixture was cooled to 5°C and cyclohexanecarbonylchloride (2.4 g, 0.016 M) and 50% sodium hydroxide (1.3 g, 0.016 M) were added separately and simultaneously so as to maintain the reaction temperature below 10°C. After the addition, the reaction mixture was allowed to warm to room temperature and stirred for 1 hr. The mixture was diluted with hexane and the solid product isolated by filtration. This product (1.5 g, 0.008 M) was dissolved in a stirred mixture of toluene (30 ml) and cooled on ice. To this mixture was added benzoylchloride (1.1 g., 0.008 M) and 50% sodium hydroxide (0.6 g, 0.008 M) simultaneously. After addition, the mixture was stirred for 1/2 hr., diluted with hexane and the solid product, $N'-\underline{t}$ -butyl-N-cyclohexylcarbonyl-N'-benzoylhydrazine, isolated by filtration.

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EXAMPLE NO. 3 - Preparation of N'-t-butyl-N-valeryl-N'-benzoylhydrazine

To a stirred suspension of <u>t</u>-butylhydrazine hydrochloride (24.8 g, 0.20 mole) in toluene (150 ml) at 5°C was added one equivalent of NaOH, prepared by diluting 16 g of 50% aqueous (aq.) NaOH to 30 ml. After addition, valeryl chloride (24 g, 0.2 mole) and another one equivalent of NaOH solution (30 ml) were dropwise added separately and simultaneously. The reaction mixture was warmed to room temperature and stirred for 40 min. The two phase mixture was separated and the organic layer was washed with water and brine. The organic layer was dried over Na₂SO₄ and

concentrated under vacuum to give a colorless oil.

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To a stirred solution of 1-t-buty1-2-valery1-hydrazine (4 g, 0.023 M) in toluene (40 ml) at 5°C was added benzoylchloride (3.4 g, 0.024 M) and 50% aq. sodium hydroxide (0.98 g, 0.024 M). After addition, the mixture was warmed to room temperature and stirred 2.5 hr. The mixture was diluted with ethyl acetate (50 ml) and washed with water (2 x 25 ml) and brine (1 x 25 ml). The organic layer was dried over magnesium sulfate and concentrated under vacuum to afford N'-t-butyl-N-valeryl-N'-benzoylhydrazine as a yellow oil.

EXAMPLE NO. 9 - Preparation of N'-t-butyl-N-phenyl-acetyl-N'-benzoylhydrazine

To a stirred suspension of \underline{t} -butylhydrazine 15 hydrochloride (2.0 g, 0.016 M) in toluene (30 ml) was added 50% sodium hydroxide (1.3 g, 0.016 M). After 15 minutes, the mixture was cooled to 5°C and phenylacetyl chloride (2.4 g, 0.016 M) and 50% sodium hydroxide (1.3 g, 0.016 M) were added separately and 20 simultaneously so as to maintain the reaction temperature below 10°C. After the addition, the reaction mixture was allowed to warm to room temperature and stirred for 1 hr. The mixture was diluted with hexane and the solid product isolated by 25 filtration. This product (3.2 g, 0.015 M) was dissolved in a stirred mixture of toluene (30 ml) and cooled on ice. To this mixture was added benzoylchloride (2.2 g, 0.016 M) and 50% sodium hydroxide (1.3 g, 0.016 M) simultaneously. After addition, the 30 mixture was stirred for 1/2 hr., diluted with hexane and the solid product, $N'-\underline{t}$ - butyl-N-phenylacetyl-N'benzoylhydrazine, isolated by filtration.

EXAMPLE NO. 11 - Preparation of N'-t-butyl-N-cyclohexenylcarbonyl-N'-benzoylhydrazine

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To a stirred suspension of t-butylhydrazine hydrochloride (0.086 g, 0.007 M) in toluene (30 ml) was added 50% sodium hydroxide (0.55 g, 0.007 M). After 15 minutes, the mixture was cooled to 5°C and cyclohexenylcarbonyl chloride (1.0 g, 0.007 M) and 50% sodium hydroxide (0.55 g, 0.007 M) were added separately and simultaneously so as to maintain the reaction temperature below 10°C. After the addition, the reaction mixture was allowed to warm to room temperature and stirred for 1 hr. The mixture was diluted with hexane and the solid product isolated by filtration. This product (1.2 g, 0.006 M) was dissolved in a stirred mixture of toluene (30 ml) and cooled on ice. To this mixture was added benzoylchloride (1.0 g, 0.007 M) and 50% sodium hydroxide (1.3 g, 0.007 M) simultaneously. After addition, the mixture was stirred for 1/2 hr., diluted with hexane and the solid product, N'-t-butyl-N-cyclohexenylcarbonyl-N'-benzoylhydrazine, isolated by filtration.

EXAMPLE NO. 14 - Preparation of N'-t-butyl-N-(beta-chloropivaloyl)-N'-benzovlhydrazine

To a stirred suspension of tert-butylhydrazine hydrochloride (200 g, 1.61 mole) in acetone (400 ml) was dropwise added triethylamine (200 g, 1.98 mole). After addition, the mixture was refluxed for 3 hours while periodically adding magnesium sulfate (100 g total). The mixture was cooled to room temperature and funnel filtered. The filtrate was dried over magnesium sulfate and concentrated under vacuum at 5°C until a slurry formed. The mixture was diluted with ethyl acetate (100 ml) and was filtered. The filtrate was distilled yielding a yellow oil (b.p. 121-127°C).

Into a stirred suspension of 1-t-buty1-2-acetone-hydrazone (43 g, 0.34 mole) in toluene (250 ml) at 5°C was added 10% aq. sodium hydroxide (200 ml, 0.50 mole). After addition, benzoylchloride (70 g, 0.50 mole) was added dropwise to this mixture. Stirring was continued for 2 hours at 5°C and 72 hours at room temperature. The mixture was diluted with ethyl acetate (300 ml) and washed with water (3 x 200 ml) and brine (200 ml). The organic layer was dried over magnesium sulfate and concentrated at 35°C under vacuum to afford a yellow oil.

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A mixture of 1-t-buty1-1-benzoy1-2-acetone hydrazone (90 g, approximately 60% pure, approximately 0.3 mole), ethanol (500 ml, 200 proof) and 10% aq. hydrochloric acid (500 ml) was stirred overnight at room temperature. The mixture was concentrated under vacuum to a thick slurry. The slurry was suction filtered with a water wash (400 ml). The solids were air-dried overnight.

The solids were dissolved in a water (200 ml) and methanol (100 ml) solution on a steam bath. mixture stood at room temperature overnight. mixture was suction filtered and rinsed with cold water (100 ml) and the solids were air dried overnight. solids were dissolved in 10% aq. hydrochloric acid (300 ml) and were washed with ethyl acetate (3 \times 300 ml). The ethyl acetate washes were combined and extracted with 10% aq. hydrochloric acid (250 ml). The 10% ag. hydrochloric acid layers were combined and were neutralized with 50% ag. sodium hydroxide while being stirred. Stirring was continued for 1 hour at room temperature. The mixture was suction filtered and rinsed with water (100 ml) and the solids were air-dried yielding a white solid (m.p. 125-126°C).

To a stirred solution of $1-\underline{t}$ -butyl-1-benzoyl-

hydrazine (1 g, 0.005 M) in toluene (40 ml) cooled to 5°C was added 3-chloro-2,2-dimethylpropionylchloride (1.2 g, 0.007 M) and 50% aq. sodium hydroxide (0.45 g, 0.0056 M) so as to maintain the temperature below 10°C. The mixture was warmed to room temperature and stirred 1 hr. The mixture was diluted with hexane (40 ml) and water (10 ml). The white solid product N'-t-butyl-N-(beta-chloropivaloyl)-N'-benzoylhydrazine was isolated by suction filtration, washed with 50 ml hexane and 50 ml water and dried.

EXAMPLE NO. 15 - Preparation of N'-t-butyl-N-(1,2,2-trichlorovinyl)carbonyl-N'-benzoylhydrazine

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hydrochloride (200 g, 1.61 mole) in acetone (400 ml) was dropwise added triethylamine (200 g, 1.98 mole). After addition, the mixture was refluxed for 3 hours while periodically adding magnesium sulfate (100 g total). The mixture was cooled to room temperature and funnel filtered. The filtrate was dried over magnesium sulfate and concentrated under vacuum at 5°C until a slurry formed. The mixture was diluted with ethylacetate (100 ml) and was filtered. The filtrate was distilled yielding a lightly yellow tinted oil (b.p. 121-127°C).

To a stirred suspension of 1-t-buty1-2-acetone-hydrazone (43 g, 0.34 mole) in toluene (250 ml) at 5°C was added 10% aq. sodium hydroxide (200 ml, 0.50 mole). After addition, benzoylchloride (70g, 0.50 mole) was added dropwise to the mixture. Stirring was continued for 2 hours at 5°C and 72 hours at room temperature. The mixture was diluted with ethyl acetate (300 ml) and washed with water (3 x 200 ml) and brine (200 ml). The organic layer was dried over magnesium sulfate and concentrated at 35°C under vacuum yielding a yellow oil.

A mixture of 1-t-butyl-1-benzoyl-2-acetone hydrazone (90 g, approximately 60% pure, approximately 0.3 mole), ethanol (500 ml, 200 proof) and 10% aq. hydrochloric acid (500 ml) was stirred overnight at room temperature. The mixture was concentrated under vacuum to a thick slurry. The slurry was suction filtered and washed with water (400 ml). The solids were air-dried overnight.

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To solids were dissolved in a water (200 ml) and methanol (100 ml) solution on a steam bath. mixture stood at room temperature overnight. mixture was suction filtered and rinsed with cold water (100 ml) and the solids were air dried overnight. solids were dissolved in 10% aq. hydrochloric acid (300 ml) and were washed with ethyl acetate (3 \times 300 ml). The ethyl acetate washes were combined and extracted with 10% aq. hydrochloric acid (250 ml). The 10% aq. hydrochloric acid layers were combined and were neutralized with 50% aq. sodium hydroxide while being stirred. Stirring was continued for 1 hour at room temperature. The mixture was suction filtered and rinsed with water (100 ml) and the solids were air-dried yielding a white solid (m.p. 125-126°C).

To a stirred solution of 1-t-butyl-1-benzoyl-hydrazine (1.5 g, 0.008 M) in methylene chloride at 5°C was added, simultaneously and separately, trichloro-acryloylchloride (1.7 g, 0.009 M) and triethylamine (0.9 g, 0.009 M). After addition, the reaction was warmed to room temperature and stirred for 3 h. The flask's contents were diluted with 50 ml methylene chloride and washed with water (3 x 75 ml) and brine solution (1 x 75 ml). The organic layer was dried over magnesium sulfate and the solvent removed under vacuum to afford N'-t-butyl-N-(1,2,2,-trichlorovinyl)carbonyl-N'-benzoylhydrazine as a white solid product.

By following substantially the procedures in processes A, B, C, D and E as exemplified above by the preparation of the compounds of Examples 1, 3, 9, 11, 14 and 15, the compounds of Formula I are prepared.

As previously noted, the compounds of the present invention exhibit excellent pesticidal activity and are selective against insects of the orders Lepidoptera and Coleoptera.

In general, for the control of insects in agriculture horticulture and forestry, a dosage corresponding to from about 10 grams to about 10 kilograms of the active substance per hectare may be used and from about 100 grams to about 5 kilograms per hectare of the active substance is preferred. exact amount of dosage for a given situation can be routinely determined and depends on a variety of factors, for example, the substance used, the kind of pest, the formulation used, the state of the crop infested with the pest and the prevailing weather conditions. The term "insecticidal" as employed in the · specification and claims of this application is to be construed as any means which adversely affects the existence or growth of the target insects. Such means can comprise a complete killing action, eradication, arresting in growth, inhibition, reducing in number or any combination thereof. The term "control" or "combat" as interchangeably employed in the specification and claims of this application is to be construed as meaning "insecticidal" or protecting plants from insect damage. By "insecticidally effective amount" is meant that dosage of active substance sufficient to exert insect "control".

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The compounds of the present invention, for practical applications, can be utilized in the form of compositions or formulations. Examples of the

preparation of compositions and formulations can be found in the American Chemical Society publication "Pesticidal Formulation Research", (1969), Advances in Chemistry Series No. 86, written by Wade Van Valkenburg; and the Marcel Dekker, Inc. publication "Pesticide Formulations", (1973), edited by Wade Van Valkenburg. In these compositions and formulations, the active substance is mixed with inert agronomically acceptable (i.e., plant compatible and/or pesticidally inert) diluents or extenders such as solid carrier material or liquid carrier material, of the type usable in conventional compositions or formulations. By agronomically acceptable carrier is meant any substance which can be used to dissolve, disperse or diffuse the active ingredient in the composition without impairing the active ingredient's effectiveness and which by itself has no significant detrimental effect on the soil, equipment, desirable plants or agronomic environment. If desired, adjuvants such as surfactants, stabilizers, antifoam agents and antidrift agents may also be added.

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Examples of compositions and formulations according to the invention are aqueous solutions and dispersions, oily solutions and oil dispersions, pastes, dusting powders, wettable powders, emulsifiable concentrates, flowables, granules, baits, invert emulsions, aerosol compositions and fumigating candles.

Wettable powders, pastes, flowables and emulsifiable concentrates are concentrated preparations which are diluted with water before or during use.

Baits are preparations generally comprising a food or other substance attractive to the target pest, that includes at least one lethal or non-lethal toxicant. Lethal toxicants kill the pest upon ingesting the bait while non-lethal toxicants change



the behaviour, feeding habits and physiology of the pest for the purpose of control.

The invert emulsions are mainly used for aerial application, where large areas are treated with a comparatively small amount of preparation. The invert emulsion may be prepared in the spraying apparatus shortly before, or even during, the spraying operation by emulsifying water in an oil solution or an oil dispersion of the active substance.

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Compositions and formulations are prepared in a known manner, for instance by extending the active compounds with conventional dispersible liquid diluent carriers and/or dispersible solid carriers optionally with the use of carrier vehicle assistants, e.g., conventional surface-active agents, including emulsifying agents and/or dispersing agents, whereby, for example, in the case where water is used as diluent, organic solvents may be added as auxiliary The following may be chiefly considered for use as conventional carrier vehicles for this purpose; aerosol propellants which are gaseous at normal temperatures and pressures, such as halogenated hydrocarbons, e.g., dichlorodifluoromethane and trifluorochloromethane, as well as butane, propane, nitrogen and carbon dioxide; inert dispersible liquid diluent carriers, including inert organic solvents, such as aromatic hydrocarbons (e.g., benzene, toluene, xylene, alkyl naphthalenes, etc.), halogenated, especially chlorinated, aromatic hydrocarbons (e.g., chlorobenzenes, etc.), cycloalkanes (e.g., cyclohexane, etc.), paraffins (e.g., petroleum or mineral oil fractions), chlorinated aliphatic hydrocarbons (e.g., methylene chloride, chloroethylenes, etc.), vegetable oils (e.g., soybean oil, cottonseed oil, corn oil, etc.), alcohols (e.g., methanol, ethanol, propanol,

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butanol, glycol, etc.) as well as ethers and esters thereof (e.g., glycol monomethyl ether, etc.), amines (e.g., ethanolamine, etc.), amides (e.g., dimethyl formamide, etc.), sulfoxides (e.g., dimethyl sulfoxide, etc.), acetonitrile, ketones (e.g., acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, isophorone, etc.), and/or water; solid carriers including ground natural minerals, such as kaolins, clays, talcs, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as highly-dispersed silicic acid, alumina and silicates; solid carriers for granules include crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, corn cobs and tobacco The following may be chiefly considered for use as conventional carrier vehicle assistants: emulsifying agents, such as cationic and/or nonionic and/or anionic emulsifying agents (e.g., polyethylene oxide esters of fatty acids, polethylene oxide ethers of fatty alcohols, alkyl sulfates, alkyl sulfonates, aryl sulfonates, albumin hydrolysates, etc., and especially alkyl arylpolyglycol ethers, magnesium stearate, sodium oleate, etc.); and/or dispersing agents, such as lignin, sulfite waste liquors, methyl cellulose, etc.

Adhesives such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polvinyl alcohol and polyvinyl acetate, can be used in the formulations.

If desired, it is possible to use colorants in compositions and formulations containing compounds of

the present invention such as inorganic pigments, for example, iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs and metal phthalocyanine dyestuffs, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

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The active compounds of the present invention may be employed alone or in the form of mixtures with one another and/or with such solid and/or liquid dispersible carrier vehicles and/or with other known compatible active agents, especially plant protection agents, such as other insecticides, arthropodicides, nematicides, fungicides, bactericides, rodenticides, herbicides, fertilizers, growth-regulating agents or synergists, if desired, or in the form of particular dosage preparations for specific application made therefrom, such as solutions, emulsions, suspensions, powders, pastes, and granules which are thus ready for use.

As concerns commercially marketed preparations, these generally contemplate carrier composition mixtures in which the active compound is present in an amount from 0.1% to 99% by weight, and preferably 1% to 75% by weight, of the mixture. Carrier composition mixtures suitable for direct application or field application generally contemplate those in which the active compound is used in an amount substantially between about 0.0001% and 5%, preferably between about 0.001% and 3%, by weight of the mixture. Thus the present invention contemplates overall formulations and compositions which comprise mixtures of a conventional dispersible carrier such as (1) a dispersible inert finely divided carrier solid, and/or (2) a dispersible carrier liquid such as an inert organic solvent and/or water, preferably including a surface-active effective

amount of a carrier vehicle assistant (e.g., a surface-active agent, such as an emulsifying agent and/or a dispersing agent), and an amount of the active compound generally between about 0.0001% and about 99% by weight of the composition, preferably 0.001% to 90% by weight of the composition, and most preferably 0.01% to 75% by weight of the composition which is effective for the purpose in question.

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The active compounds can be applied as sprays by methods commonly employed, such as conventional high-gallonage hydraulic sprays, low gallonage sprays, ultra-low-volume sprays, airblast spray, aerial sprays, and dusts. If low volume applications are desired, a solution of the compound is usually used. ultra-low-volume applications, a liquid composition containing the active compound is usually applied as a spray (e.g., mist) by means of atomizing equipment in finely divided form (average particle size of from about 50 to about 100 microns or less) using airplane crop spraying techniques. Typically only a few liters per hectare are needed and often amounts up to about 15 to 1000 g/hectare, preferably about 40 to 600 g/hectare are sufficient. With ultra-low-volume, it is possible to use highly concentrated liquid compositions with said liquid carrier vehicles containing from about 20 to about 95% by weight of the active compound.

Furthermore, the present invention contemplates methods of selectively killing, combating or controlling pests, which comprises contacting insects with a corresponding combative or toxic amount (i.e., an insecticidally effective amount) of at least one active compound of the invention alone or together with a carrier vehicle (composition or formulation) as noted above. The term "contacting" as employed in the specification and claims of this application is to be

construed as applying to at least one of (a) such insects and (b) the corresponding habitat thereof (i.e., the locus to be protected, for example, to a growing crop or an area where a crop is to be grown) the active compound of this invention alone or as a constituent of a composition or formulation. The instant formulations or compositions are applied in the usual manner, for instance by spraying, atomizing, vaporizing, scattering, dusting, watering, squirting, sprinkling, pouring, fumigating, dry dressing, moist dressing, wet dressing, slurry dressing, encrusting and the like.

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It will be realized, of course, that the concentration of the particular active compound utilized in admixture with the carrier vehicle will depend upon such factors as the type of equipment employed, method of application, area to be treated, types of pests to be controlled and degree of infestation. Therefore, in special cases it is possible to go above or below the aforementioned concentration ranges.

Granular preparations are produced for example, by taking up the active substance in a solvent and by using the resulting solution, as the case may be in the presence of a binder, to impregnate a granular carrier material, such as porous granules (for example, pumice and attaclay), or chopped tobacco stems or the like.

A granular preparation (frequently termed a "pellet") may alternatively be produced by compressing the active substance together with powdered minerals in the presence of lubricants and binders and by disintegrating and straining the composite to the desired grain size.

Dusts are obtainable by intimately mixing the active substance with an inert solid carrier material

in a concentration of from about 1 to about 50% by weight. Examples of suitable solid carrier materials are tale, kaolin, tipe clay, diatomaceous earth, dolomite, gypsum, chalk, bentonite, attapulgite and colloidal SiO₂ or mixtures of these and similar substances. Alternatively organic carrier materials such as, for example, ground walnut shells may be used.

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Wettable powders and flowables are produced by mixing from about 10 to about 39 parts by weight of a solid inert carrier such, for example, as the aforementioned carrier materials with from about 1 to about 30 parts by weight of the active substance optionally dissolved in a volatile solvent such as acetone, from about 1 to about 5 parts by weight of a dispersing agent such, for example, as the lignosulfonates or alkylnaphthalene sulfonates known for this purpose and preferably also from about 0.5 to about 5 parts by weight of a wetting agent, such as fatty alcohol sulfates, or alkylarylsulfonates of fatty acid condensation products. In the case of flowables, a liquid inert carrier such as water is also included.

To produce emulsifiable concentrates the active compound is dissolved or finely divided in a suitable solvent which preferably is poorly miscible with water, an emulsifier being added to the resulting solution. Examples of suitable solvents are xylene, toluene, high-boiling aromatic petroleum distillates, for example solvent naphtha, distilled tar oil and mixtures of these liquids. Examples of suitable emulsifiers are alkylphenoxypolyglycol ethers, polyoxyethylene sorbitan esters of fatty acids or polyoxyethylene sorbitol esters of fatty acids. The concentration of the active compound in these emulsifiable concentrates is not restricted within narrow limits and may vary between about 2% and about 50% by weight depending upon

toxicant solubility. A suitable liquid highly concentrated primary composition other than an emulsifiable concentrate is a solution of the active substance in a liquid which is readily miscible with water, for example, acetone, to which solution a dispersant and, as the case may be, a wetting agent are added. When such a primary composition is diluted with water shortly before or during the spraying operation an aqueous dispersion of the active substance is obtained.

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An aerosol preparation according to the invention is obtained in the usual manner by incorporating the active substance or a solution thereof in a suitable solvent in a volatile liquid suitable for use as a propellant such, for example, as a mixture of chlorine and fluorine derivatives of methane and ethane.

Fumigating candles or fumigating powders, i.e., preparations which when burning are capable of emitting a pesticidal smoke, are obtained by taking up the active substance in a combustible mixture which may, for example, comprise a sugar or a wood, preferably in the ground form, as a fuel, a substance to sustain combustion such, for example, as ammonium nitrate or potassium chlorate, and furthermore a substance for retarding combustion, for example kaolin, bentonite and/or colloidal silicic acid.

A bait preparation comprises a food or other substance attractive to pests, a carrier, the toxicant and may optionally include other substances commonly used in preparations of this kind, such as, a preservative to inhibit bacterial and fungal growth, a waterproofing agent to prevent disintegration under wet conditions and dyes or colorants as described above.

In addition to the aforementioned ingredients,

the preparations according to the invention may also contain other substances commonly used in preparations of this kind.

For example, a lubricant, such as calcium stearate or magnesium stearate, may be added to a wettable powder or to a mixture to be granulated. Furthermore, there may, for example, be added "adhesives" such as polyvinylalcohol cellulose derivatives or other colloidal materials, such as casein, to improve the adherence of this pesticide to the surface to be protected.

In its mechanical aspects therefore a process of the invention for improving the commercial value and/or profitability of vendible crops from plants whose growth is affected or likely to be affected by insects comprises (1) charging to a container, fumigation device or mechanical dissemination device an insecticidal composition of the invention as hereinbefore described (2) using the container, fumigator or mechanical dissemination device to apply the insecticidal composition, in the form of granules, dust, smoke, vapour or surfactant-containing liquid preparation to growing plants or to a growth medium where the plants are growing or are to be grown, or to the insects themselves, (3) controlling the dose of the active ingredient during this application step so that the rate of application of active insecticidal compound is sufficient to combat the insects but is insufficient to cause an unacceptably adverse effect on the crop plants growing or to be grown in the treated area.

Representative preparation of compositions and formulations including the compounds of the present invention are set forth below as Examples A through I by way of illustration but not limitation.

5	Example A	
	Granular	
	Ingredient	%/wt.
	Toxicant and toxicant impurities	0.25
	Triton X-305 (binder)	0.25
10	(Octylphenyl-30-ethylene	
	oxide ethanol)	
	Agsorb 24/48 (diluent)	99.50
	(Montmorillonite clay)	

Preparation: The toxicant and Triton X-305 are dissolved into methylene chloride and the mixture is added to the Agsorb with continuous mixing. The methylene chloride is then allowed to evaporate.

Example B Dust

20	Ingredient	%/wt.
	Toxicant and toxicant impurities	1.0
	Talc	99 0

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Preparation: Toxicant is dissolved in excees acetone and the mixture is impregnated onto the talc. The acetone is then permitted to evaporate.

Example C

Wettable Powder

	Ingredient	3/wt.
	Toxicant and toxicant impurities	31.3
5	Duponal WA Dry (wetter)	2.0
	(Sodium lauryl sulfate)	
	Reax 45A (dispersant)	5.0
	(Sodium lignin sulfonate)	
	Barden clay (diluent)	31.7
10	HiSil 233 (diluent)	30.0
	(Sodium silica)	

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Preparation: The toxicant, optionally dissolved in a volatile solvent, is absorbed onto the Barden clay and HiSil carriers. The Duponal and Reax are then added and the entire dry mixture blended until homogenous. The composition is then micronized to a fine particle size.

Example D

Emulsifiable Concentrate

	Emdisiliable Concentrate	
20	Ingredient	8/wt.
	Toxicant and toxicant impurities	15.0
	Sponto 232T (emulsifier)	6.0
	(Anionic and nonionic blend of	
	the following surfactants:	
25	calcium dodecyl benzene sulfonate;	
	and ethoxylated alkylphenol)	
	Sponto 234T (emulsifier)	4.0
	(Anionic and nonionic blend of	
	the following surfactants:	•
30	calcium dodecyl benzene sulfonate;	:
	and ethoxylated alkylphenol)	
	Cyclohexanone (solvent)	22.5

Tenneco 500-100 (solvent) 52.5

(Aromatic solvent mixture

principally comprising xylene,

cumene and ethyl benzene having

a boiling point range of 290-345°F)

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Preparation: All ingredients are mixed together with continuous agitation until a homogenous clear solution is obtained.

Example E

10 Aerosol

Ingredient	%/wt.
Toxicant and toxicant impurities	0.5
Freon 12	99.5

Preparation: The components are mixed and packaged under pressure in a suitable container equipped with a release spray valve.

Example F

	Fumigating Candle or Fumigating Po	owder
	Ingredient	8/wt.
20	Toxicant and toxicant impurities	1.0
	Wood dust	96.0
	Starch	3.0

Preparation: Toxicant, wood dust, and starch are blended together and then molded into a candle using a small amount of water to activate the starch.

Example G

Bait

Method A

	Ingredient	<u>%/</u> wt.
5	Toxicant and toxicant impurities	1.00
	Wheat Bran (carrier and attractant)	89.95
	Corn Syrup (attractant)	7.00
	Corn Oil (attractant)	2.00
	Kathon 4200 (preservative)	0.05
10	(3-isothiazolone)	

Preparation: The corn oil and corn syrup are added to the wheat bran with adequate mixing. The toxicant and Kathon are premixed with excess acetone and this solution is added to the wheat bran base with continued mixing. The acetone is then permitted to evaporate.

Method B

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Ingredient	3/wt.
Toxicant and toxicant impurites	0.06
Granulated Sugar (carrier and attractant)	99.94

Example H

Pellet

Same as Example G, Method A, with this addition: the bait composition is formed into 1/4" diameter by 3/8" long pellets using a suitable die and press apparatus.

Example I Flowable

	Ingredient	%/wt.
	Toxicant and toxicant impurities	31.3
5	Duponal WA Dry (wetter)	2.0
	(Sodium lauryl sulfate)	
	Reax 45A (dispersant)	5.0
	(Sodium lignin sulfonate)	
	HiSil 233 (diluent)	30.0
10	(Sodium silica)	
	Kelzan (thickener)	0.5
	(Xanthan gum)	31.2

Preparation: The toxicant is absorbed onto the HiSil carrier. The Duponal and Reax are then added and the entire dry mixture blended until homogeneous. The composition is then micronized to a fine particle size. The resulting powder is suspended in water and the Kelzan added.

Compositions and formulations according to the present invention may also include known pesticidal compounds. This expands the spectrum of activity of the preparations and may give rise to synergism.

The following known insecticidal, fungicidal and acaricidal compounds are suitable for use in such a combined preparation.

Insecticides such as:

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Chlorinated hydrocarbons, for example, 2,2-bis(p-chlorophenyl)-1,1,1-trichloroethane and hexachloroepoxyoctahydrodimethanonnaphtalene;
Carbamates, for example, N-methyl-1-naphthylcarbamates;
Dinitrophenols, for example, 2-methyl-4,6-dinitrophenyl and 2-(2-butyl)-4,6-dinitrophenyl-3,3-dimethyl-acrylate;

	Organic phosphorus compounds, such as dimethyl-2-
	methoxy-3-carbonyl-1-methylvinyl phosphate,
	O,O-diethyl-G-g-nitrophenylphosphorothicate;
	N-monomethylamide of C,O-dimethyldithio-
5	phosphorylaceric acid;
	Diphenylsulfides, for example, p-chlorobenzyl or
	p-chlorophenyl sulfide and 2,4,4',5-tetra-
	chlorodiphenylaulfide;
10	Diphenylsulfonates, for example, p-chlorophenylbenzene- sulfonate;
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	Methylcarbinols, for example, 4.4-dichloro-1-trichloro-methylbenzhydrol;
	Quinoxaline compounds, such as methylquinoxaline
	dithiocarbonate;
15	Amidines such as N'-(4-chloro-2-methylphenyl) N,N-
	dimethylformamidine;
•	Pyrethroids such as Allethrin;
	Biological such as Bacillus thuringiensis preparations;
	Organic tin compounds such as tricyclohexyltin
20	hydroxide;
٠	Synergists such as piperonyl butoxide.
	Fungicides such as:
	Organic mercury compounds, for example, phenylmercury-
	acetate and methylmercurycyanoguanide;
25	Organic tin compounds, for example, triphenyltin
	hydroxide and triphenyltin acetate;
	Alkylenebisdithiocarbamates, for example, zinc
	ethylene- bisthiocarbamate and manganese
	ethylenebisdithio-carbamate; and
30	2,4-dinitro-6-(2-octyl-phenylcrotonate), 1-bis(dimethyl
	amino)phosphoryl-3-phenyl-5-amino-1,2,4-triazole
	6-methylquinoxaline-2,3-dithiocarbonate, 1,4-
	dithio-anthraquinone-2,3-dicarbonitrile, N-
	trichloromethylthiophthalimide, N-trichloro-

methylthiotetrahydrophthalimide, N-(1,1,2,2-tetrachloroethylthio)-tetrahydrophthalimide, N-dichlorofluoromethylthio-N-phenyl-N'-dimethyl-sulfonyldiamide and tetrachloroisophthalonitrile.

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It has been found by biological evaluation that compounds according to the present invention have pesticidal activity and are capable of controlling larvae and adult forms of pests, especially insects from the orders Lepidoptera and Coleoptera. One skilled in the art will know how to determine the activity of a given compound against a given insect and the dosage required.

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As previously noted, the compounds of the present invention are particularly suitable for controlling plant-destructive insects in crops of cultivated plants, such as, but not limited to, cotton, vegetables, corn and other cereals, and the like; forestry, such as, but not limited to, birch, spruce, pine, fir, and the like; and ornamental plants, flowers and trees. Compounds of the present invention are also particularly suitable for controlling insects destructive to stored commodities such as seeds and the like; fruit crops, such as, but not limited to, fruit and/or citrus trees, raspberry bushes, and the like; and turf, such as, but not limited to, lawns, sod and the like.

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In evaluating the pesticidal activity of the compounds of this invention, the following test procedures were employed.

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A test solution containing 600 parts per million (ppm) was made by dissolving the test compound in a solvent (acetone:methanol, 1:1), adding water to give an acetone:methanol:water system of 5:5:90 and then a surfactant. A 1:1 mixture of an alkylarylpolyether-

alcohol (sold under the trademark triton N-106) and a modified phthalic glycerol alkyl resis (sold under the trademark Triton 6-1956) was utilized at the equivalent of 1 ounce per 100 (al. of test solution as a surfactant.

Initial evaluations were made on one or more of the following pests:

	Code <u>Symbol</u>	Common Name	Latin Fame
10	SAW	Southern Armyworm	Spedoptera eridania
	MBB	Mexican Bean Seetle	Epilachna varivestis

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For the foliar bean beetle and armyworm tests, individual bean (<u>Phaseolus limensis</u> var. Woods' Prolific) leaves are placed on moistened pieces of filter paper in Petri dishes. The leaves are then sprayed with the test solution using a rotating turntable and allowed to dry. The dishes are infested with 10 third instar larvae of Southern armyworm or Mexican bean beetle. The dishes are then covered.

The percent mortality for the bean beetle and armyworm evaluations are determined 96 hours after treatment. Evaluations are based on a scale of 0-100% in which 0 equals no activity and 100 equals total kill.

The rotating turntable consists of a fixed, continuously operating spray nozzle under which targets are rotated at a fixed speed and distance. When the target is a Petri dish (such as for the armyworm), the distance from the nozzle is 15 inches. The nozzle is located 8 inches from the rotating shaft. The targets on individual platforms revolve around the shaft at 1 revolution per 20 seconds but only a brief portion or this time occurs in the spray path. Targets pass only

once under the nozzle and then are removed to drying hoods.

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The nozzle used is a 1/4 JCO Spraying Systems (Wheaton, Illinois) air atomizing nozzle equipped with a No. 2850 fluid cap and No. 70 air cap. At the 10 psig air pressure used and with liquid siphon feed 0.5 GPH (gallons per hour) are delivered in a round spray pattern with a 21° spray angle. Targets are misted with spray droplets to the point that the droplets coalesce to form a uniform thin film insufficient to drown test organisms.

All treatments are maintained at 75-80°F under continuous fluorescent light in a well-ventilated room.

For soil treatment (systemic) trials, a portion of the 600 ppm test solution is diluted to 150 ppm. Ten (10) ml of the 150 ppm test solution is pipetted into soil (approximately 200 g of standard greenhouse soil) in a 3-inch pot containing a lima bean seedling. This results in a soil concentration of approximately 8 Treated plants are maintained under existing greenhouse conditions for one week. Two bean leaves are removed and placed individually on moist filter paper in Petri dishes. One leaf is infested with 10 third instar larvae of Mexican bean beetle. leaf is infested with 10 third instar larvae of Southern armyworm. The dishes are then covered and held for 3 days at which time the percent control (mortality) is determined. A second observation may be made 6 days after infesting the dishes if the experimenter feels the effect may not be complete or moribund insects appear to evidence signs of some recovery. Where necessary, untreated bean leaves are introduced into dishes held for a second observation to preclude insect starvation.

The results of the initial insecticidal

evaluations are given in Table II.

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Armyworm and been beetle spray (foliar) results are 96 hour observations. Soil treatment results are 72 hour observations. At the discretion of the experimenter, particular evaluations were held for 144 hour observations. If, after 144 hours, there was a change in the percent control, it is shown in parentheses.

TABLE II Biological Evaluations

	•	Foliar	Application	Soil App	lication	
		Tes	t Species	Test Species		
	Example No.	SAW	MBB	MBB	SAW	
	1	100	0	20	100	
15	2	100	. 60	20	40 (50)	
	3	70	100	30 (20)	40(100)	
	4	100	40	40	0 (80)	
	5	0	10	0 (40)	0 (20)	
	6	90	60	80 (60)	0 (20)	
20.	7	20	10 .	0 (40)	40 (60)	
	8	0	0	Ö(20)	0	
	9 .	70	100	20 (40)	0	
	10	80	70	40 (100)	40 (80)	
	11	100		0	100	
25	12	30	0	0	0	
	13	0	90	80 (100)	0	
	14	0	80	0 (80)	0	
	15	0	70	0	0	
	16	100	20	0	0	
30	17	70	40	0	0	
	18	100	0	•-	_1	
•	19	0	0	0	0	
	20	60	30	0 (20)	0	

No data reported.

Further examples of compounds which were prepared generally according to the above Procedures A to E were as follows:

TABLE III

5	Ex.	<u>x</u>	<u>x'</u>	R ¹	A	B	m.p. °C
	21	0	0	-C (CH ₃) ₃	A	-C ₆ H ₄ CH ₃ -3	190-192
	22		0	-С (СH ₃) ₃	$\sum_{\mathcal{O}}$	-C ₆ H ₄ CH ₃ -3	160-162.5
10	23	0	0	-C (CH ₃) ₃	С -СН ₂ С-О-СН ₂ СН ₃	$-C_6^{H_4^{Cl}_2-3,4}$	110-112
	24	0	0	-C (CH ₃) 3	-сн-с-о-сн ₂ сн ₃ -сн ₂ он	-C ₆ H ₄ Cl ₂ -3,4	low melting solid
15 '	25	0	0	-с (СН ₃) 3	CH ₂ CH ₃ CH ₃	-С ₆ ^н 4 ^{Сн} 3-3	oil
	26	0	0	-С (СН ₃) 3	-CH=CHCH ₂ CH ₃	-C ₆ H ₄ CH ₃ -3	144-146
	27	0	0	-C (CH ₃) 3	-CH ₂ CH ₂ CH=CH ₂	-C ₆ H ₄ CH ₃ -3	110-115
20	28	0	0	-C (CH ₃) ₃	-сн ₂ сн ₂ соси ₃	-C ₆ H ₄ CH ₃ -3	oil
	29	0	0	-C (CH ₃) ₃ .	-CH (CH ₃) ₂	-C ₆ H ₃ (CH ₂) ₂ -3,5	136-138
	30	0	0	-c (CH ₃) ₃	CH ₃ C II CH ₂	-C ₆ H ₃ (CII ₂) ₂ -3,5	155-163
25	31	0	0	-C (CH ³) ³	-CH (CH _{.3}) ₂	-C ₆ H ₄ Br-2	160-162

	Ex.	<u>x</u>	<u>X'</u>	R ¹	Λ	В	m.p. °C
	32	0	0	-C (CH ₃) ₃	-CH (CH ₃) ₂	-C6H5	129-131
5	33	0	0	-C (CH ₃) 3	OH	-C ₆ H ₄ CH ₃ -3	glass
	34	0	0	-С (СН ₃) 3	CH	-C ₆ H ₄ CH ₃ -3	glass
10	35	0	0	-C (CH ₃) 3	OCH3		oil
_	36	0	0	-C (CH ₃) ₃	CH3 CH3	-с ₆ н ₄ сн ₃ -з	207–210

Biological evaluation of these further Examples by the above described procedures gave the following results:

TABLE IV

5		Foliar	Foliar Application Test Species		
		Test			
	Example No.	SAW	MBB		
•	21	100	0		
	22	100	0		
10	23	0	20		
	24	. 0	30		
	2.5	90	40		
	26	100	30		
	27	100	100		
15	28	20	40		
	29	100	50-		
	30	100	30		
	31	0	80		
	32	0	40		
20	33 .	50	30		
	34	100	30		
	35	100	10		
	36	100	100		

The following words are trademarks which may or may not be registered in some or all of the designated states:

Triton, Agsorb, Duponal, Reax, HiSil, Sponto, Tenneco, Kathon and Kelzan.

CLAIMS:

An insecticidal compound having the formula:

wherein

X and X' are the same or different O, S or NR; R^1 is unsubstituted (C_3-C_{10}) branched alkyl or (C_1-C_4) straight chain alkyl substituted with one or two of the same or different (C_3-C_6) cycloalkyl;

A is unsubstituted or substituted (C_1-C_{10}) alkyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH₂, NHZ or NZZ';

unsubstituted or substituted (C_3-C_8) cycloalkyl or (C_3-C_8) cycloalkyl- (C_1-C_4) alkyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, (C_1-C_4) -alkoxy, halo- (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkanoyl, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NHZ or NZZ';

unsubstituted or substituted (C_2-C_8) alkenyl or unsubstituted or substituted (C_2-C_8) - alkadienyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, (C_3-C_6) cycloalkyl, halo- (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) -

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alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, MH_2 , MHZ or MZZ';

unsubstituted or substituted (C_3-C_8) cycloalkenyl or unsubstituted or substituted (C_3-C_8) cycloalkadienyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH₂, NHZ or NZZ';

unsubstituted or substituted (C_2-C_3) alkynyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo- (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH₂, NHZ or NZZ'; or

phenalkyl having one to four carbon atoms in the alkyl group and the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, cyano (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, (C_2-C_6) alkenyl, halo (C_2-C_6) alkenyl, NH2 or NZZ';

B is unsubstituted or substituted naphthyl where the substituents can be from one to three of the same or different halo; cyano; nitro; hydroxy; (C₁-C₄)alkoxy; (C₁-C₄)-

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alkyl; carboxy; (C₁-C₄)alkoxy-carbonyl; (C₁-C₄)alkanoyloxy; NH₂, NHZ or NZZ';

unsubstituted or substituted phenyl where the substituents can be from one to five of the same or different halo; nitro; cyano; hydroxy; (C_1-C_6) alkyl; halo (C_1-C_6) alkyl; cyano(C₁-C₆)alkyl; (C₁-C₆)alkoxy; halo- (C_1-C_6) alkoxy; alkoxyalkyl having independently 1 to 6 carbon atoms in each alkyl group; alkoxyalkoxy having independently 1 to 6 carbon atoms in each alkyl group; -OCO₂R group; (C₂-C₆)alkenyl optionally substituted with halo, cyano, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkoxy or (C₁-C₄)alkylthio; -RCO₂R' group; -COR group; halo(C₁-C₆)alkyl-carbonyl; cyano($C_1 - C_6$) alkyl-carbonyl; nitro($C_1 - C_6$)alkyl-carbonyl; $-CO_2R$ group; halo (C_1-C_6) alkoxy-carbonyl; -OCOR group; -NRR' group; amino substituted with hydroxy, (C_1-C_4) alkoxy or (C_1-C_4) alkylthio groups; phenylamino; diphenylamino; -CONRR' group; -OCONRR' group; -NRCOR' group; -NRCO2R' group; -N(COR)COR' group; -OCONRCOR' group; sulfhydryl; halothio; (C₁-C₆)alkylthio; halo(C_1 - C_6)alkylthio; -SOR group; -SO₂R group; phenylsulfonyl; -OSO2R group; halo-(C₁-C₆)alkylsulfonyloxy; -SO₂NRR' group; -NRSOR' group; -NRSO2R' group; -CSR group; -CS₂R group; -NRCSR' group; -SCOR group; unsubstituted or substituted phenyl having one to three of the same or different halo, cyano, nitro, hydroxy (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) -

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alkoxy-carbonyl, (C1-C4) alkanoyloxy, NH2 group; NHZ group; or NZZ' group; phenoxy where the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, (C_1-C_3) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH, group; NHZ group; or NZZ' group; phenylthio where the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_1) alkyl, (C_1-C_4) alkoxy, carboxy, (C₁-C₄) alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, NH₂ group; NHZ group; or NZZ' group; or when two adjacent positions on the phenyl ring are substituted with alkoxy groups, these groups may be joined to form, together with the carbon atoms to which they are both attached, a 5 or 6 membered dioxolano or dioxano heterocyclic ring;

where R, R' and R" are hydrogen or (C₁-C₆)alkyl; Z and Z' are (C₁-C₄)alkyl; "amino" means NRR'; and agronomically acceptable salts thereof.

2. A compound according to claim I wherein

X and X' are O or S; and/or

R¹ is unsubstituted (C₃-C₈) branched alkyl or

(C₁-C₄) straight chain alkyl substituted with one or two of the same or different

(C₃-C₄) cycloalkyl; and/or

A is unsubstituted or substituted (C_1-C_6) alkyl having one to three of the same or

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different halo, cyano, nitro, (C_1-C_4) alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH_2 , NHZ or NZZ';

(C₃-C₆)cycloalkyl;

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 (C_2-C_6) unsubstituted or substituted alkenyl having one to three of the same or different halo, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, (C_1-C_4) alkoxy, or halo (C_1-C_4) alkoxy;

(C3-C6)cycloalkenyl; or

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phenalkyl having one or two carbon atoms in the alkyl group and the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, nitro or (C₁-C₄)alkyl; and/or

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B is unsubstituted naphthyl; or

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unsubstituted or substituted phenyl where the substituents can be from one to three of the same of different halo; nitro; cyano; (C_1-C_4) alkyl; halo (C_1-C_4) alkyl; cyano(C_1-C_4) alkyl; (C_1-C_4) alkoxy; alkoxyalkyl having independently 1 to 4 carbon atoms in each alkyl group; -COD4 group; carboxy; (C_1-C_4) alkoxy-carbonyl; (C_1-C_4) alkanoyloxy; NH2; NHZ; NZZ'; (C₁-C₄)alkylthio; -CSD⁴ group; -CS₂D⁴ group; -SCOD⁴ group; unsubstituted or substituted phenyl having one to two of the

same or different halo, nitro,

 (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy,

 (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) -alkanoyloxy, NH2 or NZZ'; phenoxy where the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, nitro, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) -alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH2, NHZ or NZZ'; or when two adjacent positions on the phenyl ring are substituted with alkoxy groups, these groups may be joined to form, together with the carbon atoms to which they are attached, a 5- or 6-membered dioxolano or dioxano heterocyclic ring;

where D^4 and D^5 are hydrogen or (C_1-C_4) alkyl; z and Z' are (C_1-C_4) alkyl; and agronomically acceptable salts thereof.

A compound according to claim 2 wherein X and X' are O or S; and/or R¹ is branched (C₃-C₈)alkyl; and/or A is unsubstituted or substituted (C₁-C₆)alkyl having one to three of the same or different halo, cyano, nitro, carboxy or (C₁-C₄)alkoxy-carbonyl;

cyclohexyl;

cyclohexenyl;

unsubstituted or substituted (C_2-C_6) alkenyl having one to three of the same or different halo or (C_1-C_4) alkyl; or

benzyl where the phenyl ring is

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unsubstituted or substituted with one or two of the same or different halo, methyl or ethyl; and/or

B is unsubstituted naphthyl;

unsubstituted or substituted phenyl having one to three of the same or different halo; nitro; cyano; (C_1-C_4) alkyl; halo (C_1-C_4) alkyl; cyano (C_1-C_4) alkyl; (C_1-C_4) alkoxy; -COD⁴ group; (C_1-C_4) alkoxy-carbonyl; (C_1-C_4) alkanoyloxy; or unsubstituted or substituted phenyl having one or two of the same or different halo, nitro, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH₂, NHZ or NZZ'; where D⁴ is hydrogen or (C_1-C_4) alkyl; Z and Z' are (C_1-C_4) alkyl; and

agronomically acceptable salts thereof.

4. A compound according to claim 3 wherein

X and X' are 0; and/or

R¹ is branched (C₄-C₇)alkyl; and/or

A is unsubstituted or substituted (C₁-C₆)alkyl

having one to two of the same or different
halo;

cyclohexyl;

unsubstituted or substituted (C2-C6) alkenyl having one to three of the same or different halo, methyl or ethyl;

cyclohexenyl; or

benzyl; and/or

B is unsubstituted or substituted phenyl where the substituents can be from one to three of the same or different halo, $(C_1-C_4) \, \text{alkyl}, \ (C_1-C_4) \, \text{alkoxy}, \, \text{or halo-} (C_1-C_4) \, \text{alkyl}; \, \text{and} \\ \text{agrenomically acceptable salts thereof.}$

A compound according to claim 4 wherein X and X' are O; and/or R¹ is <u>t</u>-butyl, neopentyl (2,2-dimethylpropyl) or 1,2,2-trimethylpropyl; and/or A is (C₃-C₅) unsubstituted alkyl;

cyclohexyl;

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(C₂-C₄) unsubstituted or substituted straight chain alkenyl having one to three of the same or different chloro, bromo or methyl;

cyclohexenyl; or

benzyl; and/or

B is unsubstituted or substituted phenyl where
the substituents can be one or two of the
same or different chloro, fluoro, bromo,
iodo, methyl, ethyl, methoxy or
trifluoromethyl; and
agronomically acceptable salts thereof.

25 6. A compound according to claim 1 wherein X and X' are 0;

R¹ is t-butyl; and

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- B is phenyl and A is cyclohexyl, <u>n</u>-butyl, <u>n</u>-propyl, benzyl, 1-cyclohexenyl, dichloromethyl or trichloromethyl; or
- B is 4-chlorophenyl and A is \underline{n} -propyl or t-butyl; or
- B is 3-methylphenyl and A is norbornyl,
 cyclohex-3-enyl, 1-butenyl, 3-butenyl,
 cis-3,4-dihydroxycyclohexyl, 2,2dimethyl-3a,4,5,6,7,7a-hexahydrobenzo[d]dioxalano-5-yl, 3-acetyl-2,2-dimethylcyclobutyl-methyl or 2-methylcyclohexyl
 di-2,5-enyl; or
- B is 3,5-dimethylphenyl and A is isopropyl or l-methylethenyl.
- 7. A compound as claimed in Claim 2 wherein B is unsubstituted phenyl, 4-chlorophenyl, 3-substituted phenyl, 2-substituted phenyl or disubstituted phenyl.
- 8. An insecticidal composition comprising an insecticidal compound as claimed in any preceding claim together with agronomically acceptable diluent or carrier.
- 9. A composition according to claim 8 wherein said insecticidal compound is present at from 0.0001 to 99% by weight of the composition.
 - 10. A composition according to claim 8 wherein said insecticidal compound is present at from 0.001 to 99% by weight of the composition.
- 11. A composition according to claim 8 wherein said insecticidal compound is present at from 0.01 to 99% by weight of the composition.

- An insecticidal composition according to any of 12. claims 8 to 11 (a) additionally containing an emulsifying agent, said composition being in the form of an emulsifiable concentrate; or (b) additionally containing a dispersing agent, said composition being 5 in the form of a wettable powder; or (c) containing a liquid agronomically acceptable carrier and a dispersing agent, said composition being in the form of a flowable; or (d) in the form of a dust; or (e) additionally containing a binding agent, said 10 composition being in the form of a granule; or (f) additionally containing an attractant agent, said composition being in the form of a bait.
- 13. A method of controlling insects which comprises contacting said insects with an insecticidally effective amount of a compound according to any one of claims 1 to 7, optionally in a composition according to any of claims 8 to 12.
- 14. A method according to claim 13 wherein the
 insecticidal compound is applied to growing plants or
 an area where plants are to be grown at a dosage rate
 of 10 grams to 10 kilograms per hectare.
 - 15. A method according to claim 14 wherein the application rate is 100 grams to 5 kilograms per hectare.

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16. A method according to claim 13, 14 or 15 for killing insects from the order Lepidoptera or Coleoptera.

CLAIMS: ES

The use of an insecticidal compound having the formula:

wherein

X and X' are the same or different O, S or NR; R^1 is unsubstituted (C_3-C_{10}) branched alkyl or (C_1-C_4) straight chain alkyl substituted with one or two of the same or different (C_3-C_6) cycloalkyl;

A is unsubstituted or substituted (C_1-C_{10}) alkyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NHz or NZZ';

unsubstituted or substituted (C_3-C_8) cycloalkyl or (C_3-C_8) cycloalkyl- (C_1-C_4) alkyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkanoyl, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH2, NHZ or NZZ';

unsubstituted or substituted (C_2-C_8) alkenyl or unsubstituted or substituted (C_2-C_8) - alkadienyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, (C_3-C_6) cycloalkyl, halo- (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) - alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH2 or NZZ';

unsubstituted or substituted (C_3-C_8) cycloalkenyl or unsubstituted or substituted (C_3-C_8) cycloalkadienyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoylexy, NH₂, NHZ or NZZ';

unsubstituted or substituted (C_2-C_8) alkynyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo- (C_1-C_4) alkoxy, carboxy, (C_1-C_4) -alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH₂, NHZ or NZZ'; or

phenalkyl having one to four carbon atoms in the alkyl group and the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, cyano (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, (C_2-C_6) alkenyl, halo (C_2-C_6) alkenyl, NHz or NZZ';

B is unsubstituted or substituted naphthyl where the substituents can be from one to three of the same or different halo; cyano; nitro; hydroxy; (C₁-C₄)alkoxy; (C₁-C₄)-alkyl; carboxy; (C₁-C₄)alkoxy-carbonyl; (C₁-C₄)alkanoyloxy; NH₂, NHZ or NZZ';

unsubstituted or substituted phenyl where the substituents can be from one to five of the same or different halo; nitro; cyano; hydroxy; (C_1-C_6) alkyl; halo (C_1-C_6) alkyl; cyano(C₁-C₆)alkyl; (C₁-C₆)alkoxy; halo- (C_1-C_6) alkoxy; alkoxyalkyl having independently 1 to 6 carbon atoms in each alkyl group; alkoxyalkoxy having independently 1 to 6 carbon atoms in each alkyl group; -OCO₂R group; (C₂-C₆)alkenyl optionally substituted with halo, cyano, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkoxy or (C₁-C₄)alkylthio; -RCO₂R' group; -COR group; halo(C₁-C₆)alkyl-carbonyl; cyano(C_1 - C_6)alkyl-carbonyl; nitro(C_1 - C_6)alkyl-carbonyl; $-CO_2R$ group; halo (C_1-C_6) alkoxy-carbonyl; -OCOR group; -NRR' group; amino substituted with hydroxy, (C_1-C_4) alkoxy or (C₁-C₄)alkylthio groups; phenylamino; diphenylamino; -CONRR' group; -OCÓNRR' group; -NRCOR' group; -NRCO2R' group; -N (COR) COR' group; -OCONRCOR' group; sulfhydryl; halothio; (C₁-C₆)alkylthio; halo(C₁-C₆)alkylthio; -SOR group; -SO₂R group; phenylsulfonyl; -OSO2R group; halo-(C₁-C₆)alkylsulfonyloxy; -SO₂NRR' group; -NRSOR' group; -NRSO₂R' group; -CSR group; -CS₂R group; -NRCSR' group; -SCOR group; unsubstituted or substituted phenyl having one to three of the same or different halo, cyano, nitro, hydroxy $(C_1 - C_4)$ alkyl, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH_2 group; NHZ group; or NZZ' group; phenoxy

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where the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, $(C_1 - C_4)$ alkoxy-carbonyl, $(C_1 - C_4)$ alkanoyloxy, NH, group; NHZ group; or NZZ' group; phonylthio where the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, (C1-C2)alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH_2 group; NHZ group; or NZZ' group; or when two adjacent positions on the phenyl ring are substituted with alkoxy groups, these groups may be joined to form, together with the carbon atoms to which they are both attached, a 5 or 6 membered dioxolano or dioxano heterocyclic ring;

where R, R' and R" are hydrogen or (C_1-C_6) alkyl; Z and Z' are (C_1-C_4) alkyl; "amino" means NRR'; or an agronomically acceptable salt thereof, together with agronomically acceptable diluent or carrier, in making an insecticidal composition.

2. The use according to claim 1 of a compound or salt wherein,

X and X' are O or S; and/or R^1 is unsubstituted (C_3-C_8) branched alkyl or (C_1-C_4) straight chain alkyl substituted with one or two of the same or different (C_3-C_4) cycloalkyl; and/or

A is unsubstituted or substituted (C_1-C_6) alkyl having one to three of the same or

different halo, cyano, nitro, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH₂, NHZ or NZZ';

(C₃-C₆)cycloalkyl;

 (C_2-C_6) unsubstituted or substituted alkenyl having one to three of the same or different halo, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, (C_1-C_4) alkoxy, or halo (C_1-C_4) alkoxy;

(C3-C6) cycloalkenyl; or

phenalkyl having one or two carbon atoms in the alkyl group and the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, nitro or (C_1-C_4) alkyl; and/or

B is unsubstituted naphthyl; or

unsubstituted or substituted phenyl where the substituents can be from one to three of the same of different halo; nitro; cyano; (C_1-C_4) alkyl; halo (C_1-C_4) alkyl; cyano (C_1-C_4) alkyl; (C_1-C_4) alkoxy; alkoxyalkyl having independently 1 to 4 carbon atoms in each alkyl group; $-COD^4$ group; carboxy; (C_1-C_4) alkoxy-carbonyl; (C_1-C_4) alkanoyloxy; NH2; NZ2'; (C_1-C_4) alkylthio; $-CSD^4$ group; $-CS_2D^4$ group; $-SCOD^4$ group; unsubstituted or substituted phenyl having one to two of the same or different halo, nitro, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4)

where the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, nitro, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy, (C_1-C_4) alkoxy,

where D^4 and D^5 are hydrogen or (C_1-C_4) alkyl; Z and Z' are (C_1-C_4) alkyl

3. The use, according to claim 2, of a compound or salt wherein

X and X' are O or S; and/or

R¹ is branched (C₃-C₈)alkyl; and/or

A is unsubstituted or substituted (C₁-C₆)alkyl
having one to three of the same or
different halo, cyano, nitro, carboxy or
(C₁-C₄)alkoxy-carbonyl;

cyclohexyl;

cyclohexenyl;

unsubstituted or substituted (C_2-C_6) alkenyl having one to three of the same or different halo or (C_1-C_4) alkyl; or

benzyl where the phenyl ring is unsubstituted or substituted with one or

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two of the same or different halo, methyl or ethyl; and/or

B is unsubstituted naphthyl;

unsubstituted or substituted phenyl having one to three of the same or different halo; nitro; cyano; (C_1-C_4) alkyl; halo (C_1-C_4) alkyl; cyano (C_1-C_4) alkyl; (C_1-C_4) alkoxy; $-COD^4$ group; (C_1-C_4) alkoxy-carbonyl; (C_1-C_4) alkanoyloxy; or unsubstituted or substituted phenyl having one or two of the same or different halo, nitro, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, (C_1-C_4) alkoxy or (C_1-C_4) alkyl; (C_1-C_4)

4. The use, according to claim 3, of a compound or salt wherein

X and X' are O; and/or
R¹ is branched (C₄-C₇)alkyl; and/or
A is unsubstituted or substituted (C₁-C₆)alkyl
having one to two of the same or different

cyclohexyl;

halo;

unsubstituted or substituted (C₂-C₆)alkenyl having one to three of the same of different halo, methyl or ethyl;

cyclohexenyl; or

benzyl; and/or

- B is unsubstituted or substituted phenyl where the substituents can be from one to three of the same or different halo, $(C_1-C_4) \text{ alkyl}, \ (C_1-C_4) \text{ alkony, or halo-} (C_1-C_4) \text{ alkyl}.$
- 5. The use, according to claim 4, of a compound or salt wherein

cyclohexyl;

(C₂-C₄) unsubstituted or substituted straight chain alkenyl having one to three of the same or different chloro, bromo or methyl;

cyclohexenyl; or

benzyl; and/or

- B is unsubstituted or substituted phenyl where the substituents can be one or two of the same or different chloro, fluoro, bromo, iodo, methyl, ethyl, methoxy or trifluoromethyl.
- 6. The use, according to claim 1, of a compound or salt wherein

dichloromethyl or trichloromethyl; or

- B is 4-chlorophenyl and A is <u>n</u>-propyl or <u>t</u>-butyl; or
- B is 3-methylphenyl and A is norbornyl, cyclohex-3-enyl, 1-butenyl, 3-butenyl, cis-3,4-dihydroxycyclohexyl, 2,2-dimethyl-3a,4,5,6,7,7a-hexahydrobenzo(d)-dioxalano-5-yl, 3-acetyl-2,2-dimethyl-cyclobutyl-methyl or 2-methylcyclohexyl di-2,5-enyl; or
- B is 3,5-dimethylphenyl and A is isopropyl or 1-methylethenyl.
- 7. The use according to claim 2 of the compound or salt wherein B is unsubstituted phenyl, 4-chlorophenyl, 3-substituted phenyl, 2-substituted phenyl or disubstituted phenyl.
- 8. The use according to any preceding claim of the compound or salt in an amount of from 0.0001 to 99% by weight of the composition.
- 9. The use according to claim 8 of the compound or salt in an amount of from 0.001 to 99% by weight of the composition.
- 10. The use according to claim 8 of the compound or salt in an amount of from 0.01 to 99% by weight of the composition.
- 11. The use according to any preceding claim of the compound or salt (a) together with emulsifying agent, in making an emulsifiable concentrate; or (b) together with a dispersing agent in making a wettable powder; or (c) together with a liquid agronomically acceptable

carrier and a dispersing agent in making a flowable; or (d) in the form of a dust; or (e) together with a binding agent in making a granular formulation; or (f) together with an attractant agent in making a bait.

- 12. The use of a compound or salt as defined in any one of claims 1 to 7, optionally in a composition also containing agrenomically acceptable diluent or carrier, for controlling insects by contacting said insects with an insecticidally effective amount of the compound or salt.
- A mechanical process for improving the commercial value and/or profitability of vendible crops from plants whose growth is affected or likely to be affected by insects comprising (1) charging to a container, fumigation device or mechanical dissemination device an insecticidal compound or salt as defined in any of claims 1 to 7, optionally in a mixture with agronomically acceptable diluent or carrier, (2) using the container, fumigator or mechanical dissemination device to apply the insecticidal compound or salt, in the form of granules, dust, smoke, vapour or surfactant-containing liquid preparation to growing plants or to a growth medium where the plants are growing or are to be grown, or to the insects themselves, (3) controlling the dose of the active ingredient during this application step so that the rate of application of active insecticidal compound is sufficient to combat the insects but is insufficient to cause an unacceptably adverse effect on the crop plants growing or to be grown in the treated area.

- 14. The use or process according to claim 12 or 13 wherein the insecticidal compound or salt is applied to growing plants or an area where plants are to be grown at a dosage rate of 10 grams to 10 kilograms per hectare.
- 15. The use or process according to claim 14 wherein the application rate is 100 grams to 5 kilograms per hectare.
- 16. The use or process according to claim 13 or 14 for killing insects from the order Lepidoptera or Coleoptera.

CLAIMS: AT

1. An insecticidal composition comprising, as an active insecticidal ingredient, a compound having the formula:

wherein

X and X' are the same or different O, S or NR; R^1 is unsubstituted (C_3-C_{10}) branched alkyl or (C_1-C_4) straight chain alkyl substituted with one or two of the same or different (C_3-C_6) cycloalkyl;

A is unsubstituted or substituted (C_1-C_{10}) alkyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH2 or NZZ';

unsubstituted or substituted (C_3-C_8) cycloalkyl or (C_3-C_8) cycloalkyl- (C_1-C_4) alkyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, (C_1-C_4) -alkoxy, halo (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH₂, NHZ or NZZ';

unsubstituted or substituted (2.-0) elkery, or unsubstituted or substituted (0.-0) elkery alkadienyl having one to four of the same or different halo, cyano, sitte, hyperent (C_1 - C_4) alkyl, (C_3 - C_6) cyclealkyl, here

 (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) - alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH₂, NHZ or NZZ';

unsubstituted or substituted (C_3-C_8) cycloalkenyl or unsubstituted or substituted (C_3-C_8) cycloalkadienyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH₂, NHZ or NZZ';

unsubstituted or substituted (C_2-C_8) alkynyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo- (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH₂, NHZ or NZZ'; or

phenalkyl having one to four carbon atoms in the alkyl group and the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, cyano (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, (C_2-C_6) alkenyl, halo (C_2-C_6) alkenyl, NH2 or NZZ';

B is unsubstituted or substituted naphthyl where the substituents can be from one to three of the same or different halo; cyano; nitro; hydroxy; (C_1-C_4) alkoxy; (C_1-C_4) -alkyl; carboxy; (C_1-C_4) alkoxy-carbonyl; (C_1-C_4) alkanoyloxy; NH_2 , NHZ or NZZ';

unsubstituted or substituted phenyl where the substituents can be from one to five of the same or different halo; nitro; cyano; hydroxy; (C_1-C_6) alkyl; halo (C_1-C_6) alkyl; cyano(C_1 - C_{ϵ}) alkyl; (C_1 - C_{ϵ}) alkoxy; halo- (C_1-C_6) alkoxy; alkoxyalkyl having independently 1 to 6 carbon atoms in each alkyl group; alkoxyalkoxy having independently 1 to 6 carbon atoms in each alkyl group; -OCO₂R group; (C₂-C₆)alkenyl optionally substituted with halo, cyano, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkoxy or (C₁-C₄)alkylthio; -RCO₂R' group; -COR group; halo(C₁-C₆)alkyl-carbonyl; cyano($C_1 - C_6$) alkyl-carbonyl; nitro($C_1 - C_6$)alkyl-carbonyl; $-CO_2R$ group; halo (C_1-C_6) alkoxy-carbonyl; -OCOR group; -NRR' group; amino substituted with hydroxy, (C_1-C_4) alkoxy or (C_1-C_4) alkylthio groups; phenylamino; diphenylamino; -CONRR' group; -OCONRR' group; -NRCOR' group; -NRCO2R' group; -N(COR)COR' group; -OCONRCOR' group; sulfhydryl; halethio; (C_1-C_6) alkylthio; halo(C₁-C₆)alkylthio; -SOR group; -SO₂R group; phenylsulfonyl; -OSO₂R group; halo-(C₁-C₆)alkylsul:onyloxy; -SO₂NRR' group; -NRSOR' group; -NRSO₂k' group; -CSR group; -CS₂R group; -NRCSR' group; -SCOR group; unsubstituted or substituted phenyl having one to three of the same or different halo, cyano, nitro, hydroxy (C1-C4)alkyl,

 (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C1-C4) alkanoyloxy, NH2 group; NHZ group; or NZZ' group; phenoxy where the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH2 group; NHZ group; or NZZ' group; phenylthio where the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, NH₂ group; NHZ group; or NZZ' group; or when two adjacent positions on the phenyl ring are substituted with alkoxy groups, these groups may be joined to form, together with the carbon atoms to which they are both attached, a 5 or 6 membered dioxolano or dioxano heterocyclic ring;

where R, R' and R" are hydrogen or (C₁-C₆)alkyl; Z and Z' are (C₁-C₄)alkyl; "amino" means NRR'; or an agronomically acceptable salt thereof, together with agronomically acceptable diluent or carrier.

2. A composition according to claim 1 wherein X and X' are O or S; and/or R¹ is unsubstituted (C₃-C₈) branched alkyl or (C₁-C₄) straight chain alkyl substituted with one or two of the same or different (C_3-C_4) cycloalkyl; and/or A is unsubstituted or cunstituted (C_1-C_6) alkyl having one to three of the same or different halo, cyano, nitro, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, (C_1-C_4) NHZ or NZZ';

(C3-C6) cycloalkyl;

 (C_2-C_5) unsubstituted or substituted alkenyl having one to three of the same or different halo, (C_1-C_4) alkyl, halo (C_1-C_4) alkyl, (C_1-C_4) alkoxy, or halo (C_1-C_4) alkoxy;

(C₃-C₆)cycloalkenyl; or

phenalkyl having one or two carbon atoms in the alkyl group and the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, nitro or (C_1-C_4) alkyl; and/or

B is unsubstituted naphthyl; or

unsubstituted or substituted phenyl where the substituents can be from one to three of the same of different halo; nitro; cyano; (C_1-C_4) alkyl; halo (C_1-C_4) alkyl; cyano (C_1-C_4) alkyl; (C_1-C_4) alkoxy; alkoxyalkyl having independently 1 to 4 carbon atoms in each alkyl group; $-COD^4$ group; carboxy; (C_1-C_4) alkoxy-carbonyl; (C_1-C_4) alkanoyloxy; NH₂; NHZ; NZZ'; (C_1-C_4) alkylthio; $-CSD^4$ group; $-CS_2D^4$ group; $-SCOD^4$ group; unsubstituted or

substituted phenyl having one to two of the same or different halo, nitro, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, NH₂, NHZ or NZZ'; phenoxy where the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, nitro, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH2, NHZ or NZZ'; or when two adjacent positions on the phenyl ring are substituted with alkoxy groups, these groups may be joined to form, together with the carbon atoms to which they are attached, a 5- or 6-membered dioxolano or dioxano heterocyclic ring;

where D^4 and D^5 are hydrogen or (C_1-C_4) alkyl; Z and Z' are (C_1-C_4) alkyl.

A composition according to claim 2 wherein X and X' are O or S; and/or R¹ is branched (C₃-C₈)alkyl; and/or A is unsubstituted or substituted (C₁-C₆)alkyl having one to three of the same or different halo, cyano, nitro, carboxy or (C₁-C₄)alkoxy-carbonyl;

cyclohexyl;

cyclohexenyl;

unsubstituted or substituted (C_2-C_6) alkenyl having one to three of the same or different halo or (C_1-C_4) alkyl; or

benzyl where the phonyl ring is unsubstituted or substituted with one or two of the same or different halo, methyl or athyl; and/or

B is unsubstituted naphthyl;

unsubstituted or substituted phenyl having one to three of the same or different halo; nitro; eyano; (C_1-C_4) alkyl; halo (C_1-C_4) alkyl; cyano (C_1-C_4) alkyl; (C_1-C_4) alkoxy; $-\text{CoD}^4$ group; (C_1-C_4) alkoxy-carbonyl; (C_1-C_4) alkanoyloxy; or unsubstituted or substituted phenyl having one or two of the same or different halo, nitro, (C_1-C_4) alkyl, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, (C_1-C_4) alkyl; (C_1-C_4) alkyl; (C_1-C_4) alkyl; (C_1-C_4) alkyl; (C_1-C_4) alkyl; (C_1-C_4) alkyl.

A composition according to claim 3 wherein X and X' are 0; and/or R¹ is branched (C₄-C₇)alkyl; and/or A is unsubstituted or substituted (C₁-C₆)alkyl having one to two of the same or different halo;

cyclohexyl;

unsubstituted or substituted (C2-C6) alkenyl having one to three of the same of different halo, methyl or ethyl;

cyclohexenyl; or

benzyl; and/or

- B is unsubstituted or substituted phenyl where the substituents can be from one to three of the same or different halo, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, or halo- (C_1-C_4) alkyl.
- A composition according to claim 4 wherein X and X' are O; and/or R¹ is <u>t</u>-butyl, neopentyl (2,2-dimethylpropyl) or 1,2,2-trimethylpropyl; and/or A is (C₃-C₅) unsubstituted alkyl;

cyclohexyl;

(C₂-C₄) unsubstituted or substituted straight chain alkenyl having one to three of the same or different chloro, bromo or methyl;

cyclohexenyl; or

benzyl; and/or

- B is unsubstituted or substituted phenyl where the substituents can be one or two of the same or different chloro, fluoro, bromo, iodo, methyl, ethyl, methoxy or trifluoromethyl.
- A composition according to claim 1 wherein X and X' are O;

 R¹ is <u>t</u>-butyl; and
 B is phenyl and A is cyclohexyl, <u>n</u>-butyl,

 <u>n</u>-propyl, benzyl, 1-cyclohexenyl,

dichloromethyl or trichloromethyl; or

- B is 4-chlorophenyl and A is <u>n</u>-propyl or <u>t</u>-butyl; or
- B is 3-methylphenyl and A is norbornyl, cyclohex-3-enyl, 1-butenyl, 3-butenyl, cis-3,4-dihydroxycyclohexyl, 2,2-dimethyl-3a,4,5,6,7,7a-hexahydrobenzo(d)-dioxalano-5-yl, 3-acetyl-2,2-dimethyl-cyclobutyl-methyl or 2-methylcyclohexyl di-2,5-enyl; or
- B is 3,5-dimethylphenyl and A is isopropyl or l-methylethenyl.
- 7. A composition as claimed in claim 2 wherein B is unsubstituted phenyl, 4-chlorophenyl, 3-substituted phenyl, 2-substituted phenyl or disubstituted phenyl.
- 8. A composition according to any preceding claim wherein said insecticidal ingredient is present at from 0.0001 to 99% by weight of the composition.
- 9. A composition according to claim 8 wherein said insecticidal ingredient is present at from 0.001 to 99% by weight of the composition.
- 10. A composition according to claim 8 wherein said insecticidal ingredient is present at from 0.01 to 99% by weight of the composition.
- 11. An insecticidal composition according to any preceding claim (a) additionally containing an emulsifying agent, said composition being in the form of an emulsifiable concentrate; or (b) additionally containing a dispersing agent, said composition being in the form of a wettable powder; or (c) containing a

liquid agronomically acceptable carrier and a dispersing agent, said composition being in the form of a flowable; or (d) in the form of a dust; or (e) additionally containing a binding agent, said composition being in the form of a granule; or (f) additionally containing an attractant agent, said composition being in the form of a bait.

- 12. A method of controlling insects which comprises contacting said insects with an insecticidally effective amount of insecticidal ingredient as defined in any one of claims 1 to 6, optionally in a composition according to any preceding claim.
- 13. A method according to claim 12 wherein the insecticidal ingredient is applied to growing plants or an area where plants are to be grown at a dosage rate of 10 grams to 10 kilograms per hectare.
- 14. A method according to claim 13 wherein the application rate is 100 grams to 5 kilograms per hectare.
- 15. A method according to claim 12 or 13 for killing insects from the order Lepidoptera or Coleoptera.



SUROPEAN SEARCH REPORT

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